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CXV. *The Electronic Theory of Valency.*—I. *Intramolecular Ionization.*

By THOMAS MARTIN LOWRY *.

I. *Introductory.*

THE theory of intramolecular ionization was put forward in 1914 by Sir Joseph Thomson in a paper on "The Forces between Atoms and Chemical Affinity" (Phil. Mag. [6] xxvii. p. 757, 1914). It was based on phenomena observed with positive rays, where it was found that negatively- as well as positively-charged atoms of hydrogen, oxygen, carbon, and chlorine were present in the discharge. These must obviously have taken up at least two electrons in order to neutralize and then to reverse the positive charge with the help of which they were driven through the cathode. Opposite polarities were shown, therefore, to be possible in the atoms of many of the common elements, and it was suggested that this might also occur under more commonplace conditions.

Since it appeared that ionized molecules would have a greater electrical moment than those which were neutral throughout, it was possible in the case of gases to apply experimental tests in order to determine whether internal ionization had or had not taken place. A number of common

* Communicated by the Faraday Society.

gases were therefore classified, with the help of observations on specific inductive capacity and refractive index, into two groups, as follows :—

Group I. *Not Ionized.*	Group II. *Ionized.*
H_2, O_2, N_2, Cl_2,	HCl, CH_3Cl, $CHCl_3$ (weak),
He, CO, CO_2, CS_2,	H_2O, $CH_3 \cdot OH$, $C_2H_5 \cdot OH$,
CH_4, CCl_4, C_6H_6, N_2O.	NH_3, SO_2.

To chemists, intramolecular ionization is most familiar in the case of the organic amino-acids, such as glycine, the salt-like formula for which is justified by the conversion of glycine on methylation into betaine, which cannot pass into a non-ionized form except by addition of water.

$$NH_2 \cdot CH_2 \cdot CO \cdot OH \rightarrow \overset{+}{N}H_3 \cdot CH_2 \cdot CO \cdot \overset{-}{O} \rightarrow \overset{+}{N}Me_3 \cdot CH_2 \cdot CO \cdot \overset{-}{O}.$$

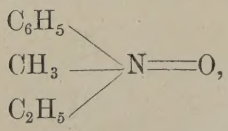
Glycine (non-ionized form). Glycine (ionized form). Betaine (ionized form).

The introduction of electronic formulæ based on the theory of octets has, however, made it necessary to postulate a condition of intramolecular ionization in a large number of compounds where nothing of the sort has been suspected previously. Thus, in the two isosteric gases, carbon dioxide and nitrous oxide, the nuclear charges and the attached electrons are found to be perfectly balanced in carbon dioxide, which Lewis represents as $:\ddot{O}::C::\ddot{O}:$, if each electron that is shared with another atom is reckoned as one-half; but in nitrous oxide, $:\ddot{O}::N::\ddot{N}:$, where the nuclear charges are $8+7+7$ instead of $8+6+8$, this balance is destroyed by the transfer of a unit of positive electricity from the nucleus of one of the outer atoms to the nucleus of the central atom of the chain. If carbon dioxide be written as $O=C=O$, nitrous oxide must then be written as $O=\overset{+}{N}=\overset{-}{N}$, or $O=N\rightleftharpoons N$, where the barb represents an electrovalency directed from the + to the — atom. In addition to its application in organic chemistry, which will form the subject of another paper, the theory of intramolecular ionization has a number of applications in inorganic chemistry, and these are set out briefly in the paragraphs which follow.

2. *Odd and Even Valencies.*

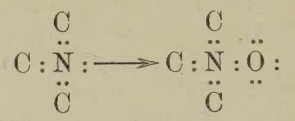
Before the advent of the octet theory, chemists were wont to divide the elements into two groups according as the typical valencies were odd or even numbers. This subdivision was based on a rule, to which there are not many exceptions, that when the valency of an element varies, it generally increases or diminishes by two units. The principal exceptions to this rule are found in nitric oxide, NO, nitrogen dioxide, NO_2, triphenylmethyl, $C(C_6H_5)_3$, and in certain cases of dissociation such as monatomic iodine, where, as Lewis points out, the total number of electrons in the molecule is an odd number. With the advent of the octet theory, it appeared that each element had, as a rule, only one principal valency, although electro-negative elements could use this either as a covalency or as an electrovalency of equal number; apart from this exception, it looked as if every case of variable valency represented an exception to the general rules of the octet theory. When, however, the possibility of "mixed" bonds is admitted, it is seen that in a large number of cases *two* units of valency may be added, namely one covalency and one electrovalency, without disturbing the arrangement of the octets on which the primary valency was based; these cases will be found to cover nearly all the instances in which Langmuir has used variable valencies in constructing electronic formulæ for inorganic compounds (J. Amer. Chem. Soc. xli. p. 868, 1919).

This effect can be demonstrated most easily in the case of oxygen, which has six electrons in its outer shell. Since a single octet contains eight and a double octet contains fourteen electrons in the outer shell, an atom of oxygen can, if other conditions are favourable, be added to any saturated octet which is not already surrounded by four other atoms or radicles. This limitation makes it impossible to increase the valency of carbon from 4 to 6 by converting methane into an oxide, since all the electrons of the octet have already been converted into duplets; but, in the case of nitrogen, saturated compounds of the ammonia-type can be converted into oxides, as in the case of the methylethylaniline oxide,

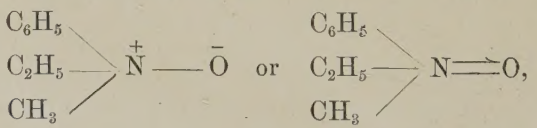


which was prepared by Meisenheimer in optically active

forms. From the point of view of the octet theory, the oxidation of the nitrogen atom in methylethylaniline is represented by the scheme

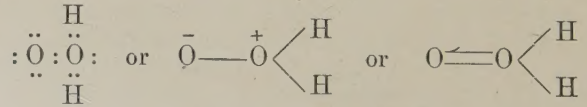


This shows the last available edge of the nitrogen octet as being gripped by an oxygen atom, Ö :, which carries with it the six electrons that are needed to add an additional octet to the system. Langmuir (J. Amer. Chem. Soc. lxii. p. 280, 1920) states definitely that in this compound "the nitrogen is quadricovalent, and it is entirely unnecessary to assume a quinquevalent nitrogen." It is difficult to believe that Langmuir can have overlooked the fact that in this system the nitrogen atom is positively charged (and thereby converted into a kation), whilst the oxygen is negatively charged, and so converted into a "bound" anion, since the two ions are united by the covalency as well as by the electrovalency; but I cannot find in any of Langmuir's papers a clear recognition of the phenomena of intramolecular ionization, or of the existence in this compound of "bound" ions corresponding with the "free" ions of ammonium chloride. It therefore really looks as if the obvious method of representing this compound as one in which the oxygen is linked to the nitrogen by a mixed double bond, including one covalency and one electrovalency, thus



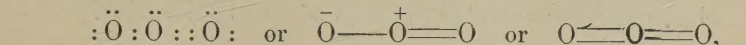
may perhaps be novel.

By bracketing the oxygen atom in a precisely similar way onto a molecule of water, a formula is obtained in which the valency of one atom of oxygen is increased from 2 to 4 just as that of the nitrogen was increased from 3 to 5 by converting methylethylaniline into its oxide. The formulæ



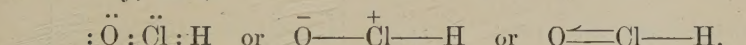
appear to represent the properties of free hydrogen peroxide

more accurately than the conventional formula which shows the compound as containing two hydroxyl groups linked by a covalency, thus HO·OH. Its close resemblance to ozone may be shown by representing the latter compound as one in which an oxygen atom is bracketed onto a molecule of oxygen, thus,

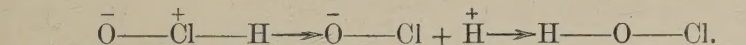


the valency of one of the oxygen atoms being again increased by two units, one of covalency and one of electrovalency.

Theoretically it should be possible to treat hydrogen chloride in the same way and to convert it into an oxy-acid in which the valency of the chlorine would be raised from 1 to 3 by the addition of one unit of covalency and one of electrovalency, thus,



In practice, however, it is clear that the ionization of this molecule would leave the anion with a negative charge on the oxygen, and that the hydrogen ion would therefore be likely to return to the oxygen rather than to the uncharged chlorine.



The formula for hypochlorous acid in its non-ionized form is therefore not H——Cl⟹O but H——O——Cl, and it is from this latter compound that any scheme for increasing the valency of chlorine in this series of acids must start. In the ion, however, as will be shown below, there is nothing to distinguish this first atom of oxygen from those which are introduced subsequently.

3. *Stability of Oxy-acids.*

The increasing stability of the oxy-acids and of their salts as the number of oxygen atoms increases appears to receive a clearer explanation than has hitherto been possible now that the phenomena can be interpreted in the light of the phenomenon of intramolecular ionization.

(a) *Oxy-acids of Chlorine.*—The complete series of chloro-acids may be set out as in Table I., which shows in the case of each ion (i.) the ordinary chemical formula, (ii.) the electronic formula, (iii.) the electronic formulæ interpreted by means of the theory of intramolecular ionization, (iv.) an

alternative representation of the mixed double bonds in which the total number of valencies can be seen more clearly than when + and − signs are used.

TABLE I.

Electronic Formulæ for the Ions of the Chloro-acids.

Name of acid.	Formula of Ion.	Electronic Formula of Ion.	Formulæ showing Mixed double Bonds.
Hydrochloric acid...	Cl'	$:\ddot{Cl}:$	$\bar{Cl}$
Hypochlorous acid..	ClO'	$:\ddot{Cl}:\ddot{O}:$	$Cl—\bar{O}$
Chlorous acid	ClO_2'	$:\ddot{O}:\ddot{Cl}:\ddot{O}:$	$\bar{O}—\overset{+}{Cl}—\bar{O}$ or $O\leftleftarrows Cl\rightrightarrows O$
Chloric acid	ClO_3'	$:\ddot{O}:$ $:\ddot{O}:\ddot{Cl}:\ddot{O}:$	$\bar{O}—\overset{++}{Cl}(—\bar{O})—\bar{O}$ or $O\leftleftarrows Cl(\rightrightarrows O)\rightrightarrows O$
Perchloric acid	ClO_4'	$:\ddot{O}:$ $:\ddot{O}:\ddot{Cl}:\ddot{O}:$ $:\ddot{O}:$	$\bar{O}—\overset{+++}{Cl}(—\bar{O})(—\bar{O})—\bar{O}$ or $O\leftleftarrows Cl(\rightrightarrows O)(\rightrightarrows O)\rightrightarrows O$

The most conspicuous feature of the formulæ in the fourth column is the progressive growth of the positive charge on the chlorine atom. This atom is originally negative, but passes through the successive stages of $\overset{+}{Cl}$, $\overset{++}{Cl}$, $\overset{+++}{Cl}$ until it carries a surplus of three positive charges. Since the oxygen in each of these compounds is negatively charged, it is clear that the stability of the oxy-acids should increase as the polarity of the central chlorine atom increases. A maximum is, however, reached in the case of perchloric acid because all the electrons of the chlorine octet are now shared with other atoms and no more oxygen atoms can be bracketed onto the chlorine.

(b) *Oxy-acids of Sulphur.*

In the case of the sulphur-acids, it is interesting to note

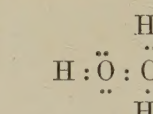
TABLE II.

Electronic Formulæ for the Ions of the Sulphur-acids.

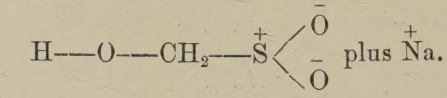
Name of acid.	Formula of Ion.	Electronic Formula of Ion.	Formula showing Mixed Double Bonds.
Sulphuretted hydrogen	S''	$:\ddot{S}:$	$\overline{\overline{S}}$
H_2SO (not known) ...	SO''	$:\ddot{S}:\ddot{O}:$	$\bar{S}—\bar{O}$
H_2SO_2 (not known) ...	SO_2''	$:\ddot{O}:\ddot{S}:\ddot{O}:$	$\bar{O}—S—\bar{O}$
Sulphurous acid	SO_3''	$:\ddot{O}:$ $:\ddot{O}:\ddot{S}:\ddot{O}:$	$\bar{O}—\overset{+}{S}—\bar{O}$ or $O\rightleftharpoons S\rightleftharpoons O$
Sulphuric acid	SO_4''	$:\ddot{O}:$ $:\ddot{O}:\ddot{S}:\ddot{O}:$ $:\ddot{O}:$	$\bar{O}—\overset{++}{S}—O$ or $O\rightleftharpoons S\rightleftharpoons O$

that the double negative charge of the sulphide ion, $\overline{\overline{S}}$, would be distributed between sulphur and oxygen in the ion of the hypothetical acid, H_2SO, whilst the ion of the acid, H_2SO_2, has both negative charges on oxygen and none on sulphur. Under these conditions, it is not surprising to find that the acid, H_2SO, the ion of which would consist of two negatively-charged atoms, appears not to be capable of existence, whilst the ion, SO_2, which would have two negatively-charged atoms of oxygen attached to a neutral atom of sulphur, is apparently of the same low order of stability as the ion ClO', where precisely similar conditions prevail. Stable ions only begin to be formed when the central sulphur atom acquires a positive charge as in the ions of the sulphites $\left(\bar{O}\diagdown\ \bar{O}\diagup\!\!>\overset{+}{S}—\bar{O}\right)$ and sulphates $\left(\bar{O}\diagdown\ \bar{O}\diagup\!\!>\overset{++}{S}\diagup\!\!<\bar{O}\ \bar{O}\diagdown\right)$. In this connexion it is of interest to note that the acid, H_2SO_2 (which is the only one to which the name of hyposulphurous

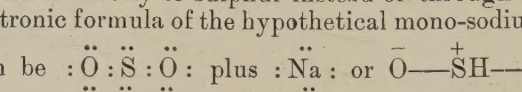
acid can be correctly applied *), although itself unknown, is manufactured on a large scale as a commercial reducing agent in the form of a condensation-product with formaldehyde, sodium formaldehyde sulphoxylate, $HO \cdot CH_2 \cdot SO \cdot ONa$. The electronic formula of this compound is, however,



or

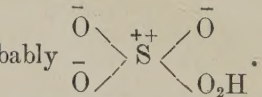


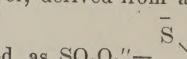
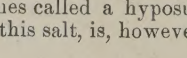
The electronic formula shows clearly that in this case also stability is only achieved when the sulphur atom has acquired a positive charge. This has, in fact, been done by treating the acid as monobasic, with one hydrogen atom attached directly to sulphur instead of through oxygen ; the electronic formula of the hypothetical mono-sodium salt would

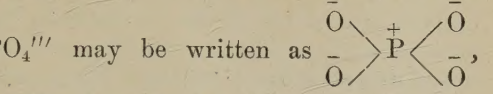
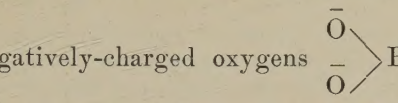
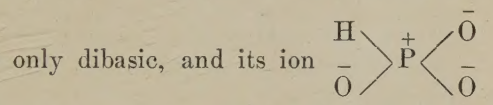
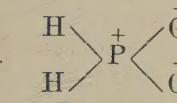
then be 

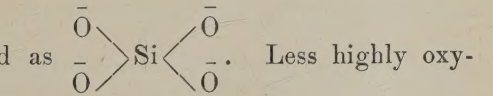
and the sulphur atom is again seen to be carrying a positive charge.

The sulphur-series of oxy-acids again stops short at a point where four oxygen atoms are linked to the central atom. A persulphuric acid of the formula H_2SO_5 is indeed known, but it is a monobasic acid, which must be formulated as a monosulphonic derivative of hydrogen peroxide, and its ion is

probably  .

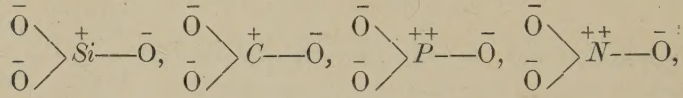
* Ordinary "hypo" was at first thought to be a real hyposulphate having the formula $NaHSO_2$, in which one of the molecules of water of crystallization was taken into the structure ($Na_2S_2O_3$, $H_2O = 2NaHSO_2$); it is, however, derived from a dibasic acid of the S_2 series, and its ion is formulated as $SO_2O_3'' =$  . Zinc hydrosulphite, which is also sometimes called a hyposulphite, was thought to be $ZnSO_2$ instead of ZnS_2O_4; this salt, is, however, also derived from a dibasic acid of the S_2 series, and its ion is formulated as  . It will be noticed that the ions of these stable compounds have, like those of the sulphites and sulphates, a positive charge on the central sulphur atoms.

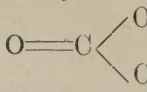
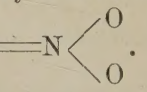
(c) *Oxy-acids of Phosphorus.*—The most stable acid of phosphorus is again the one which contains four oxygen atoms. Its ion PO_4''' may be written as  , where it is seen that the atom of phosphorus carries only a single positive charge. The corresponding acid with three atoms of oxygen would therefore have a neutral atom in the centre of three negatively-charged oxygens  , and would be of very low stability: actually, however, phosphorous acid is only dibasic, and its ion  retains a single positive charge, very much as in the case of the sulphoxylic acid, quoted under (b) above. The next acid of the series, hypophosphorous acid, H_3PO_2, behaves in a corresponding way, since this is only monobasic; its ion,  , therefore still retains the single positive charge, which appears to be essential for stability in nearly all the oxy-acids.

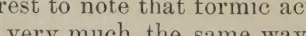
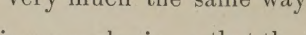
(d) *Silicic Acid.*—In the case of silicon, even the O_4 acid has a neutral atom in the centre of the ion SiO_4'''', which must be represented as  . Less highly oxygenated acids of which the ions would contain a negatively-charged silicon atom surrounded by negatively-charged oxygen atoms are unknown.

(e) *Dehydrated Acids.*—In all the above cases the formulæ assigned to the various ions agree, so far as covalencies are concerned, with the formulæ attributed to them by Langmuir; but as he failed to recognise the intramolecular ionization of these compounds, and therefore omits all the charges on the atoms, it was not possible for him to arrive at the simple theory set out above, that stability in oxy-acids usually depends on retaining a positive charge on the central

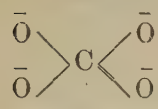
atom, without which it is difficult to hold the negatively-charged oxygen atoms. In the case of the dehydrated acids such as H_2SiO_3 and H_2CO_3, or HPO_3 and HNO_3, which are derived from acids of the O_4 series by the removal of water, satisfactory formulæ are provided most readily by assigning to the central atom a "sextet" (Lewis, J. Amer. Chem. Soc. xxxviii. p. 775, 1916; Latimer & Rodebush, ibid. lxii. p. 1429, 1920) or "depleted octet" of 8 or 16 electrons instead of the 2+8 or 2+8+8 electrons of the normal octet. The introduction of this conception has very far-reaching consequences in organic chemistry, and its introduction in inorganic chemistry appears, therefore, to be at least worthy of a trial. On this basis the ions of the four acids cited above become



where the symbols printed in italics are those of atoms which are assumed to carry two electrons less than the usual number; the much greater stability of the O_4 acids of silicon and phosphorus as compared with carbon and nitrogen may perhaps be associated with the greater difficulty of carrying out this robbery in the case of atoms containing three shells of electrons instead of two. The new formulæ have the advantage of eliminating the difference between the single and double bonds of the conventional formulæ, and replacing each by a covalence and electrovalence; they also make the formulæ of the ions symmetrical as regards the three oxygen atoms, and thus bring them into line with the crystallographic data where previously it was customary to write them unsymmetrically as *  and  .

It is of interest to note that formic acid, CH_2O_2, maintains its stability in very much the same way as hypophosphorous acid by becoming monobasic, so that the ion is  , and not  , where the central carbon atom would be neutral instead of carrying a stabilizing positive charge. This neutrality of the central atom can, of course, also be used

* The "symmetrical" formula for the nitrates was given by Latimer and Rodebush, but without the electric charges shown above.

to explain the instability of orthocarbonic acid, H_4CO_4, or  , although derivatives such as $C(OC_2H_5)_4$, in which neutral atoms are held together by covalencies, are quite stable; as shown above, the central atom of the ion acquires a positive charge when orthocarbonic acid passes into carbonic acid, and the carbonates derived from the latter acid are fairly stable.

Finally, attention may be directed to the fact that the old conception of "ortho-acids" in which all the oxygen is present as hydroxyl, *e. g.* $Si(OH)_4$, $P(OH)_5$, $S(OH)_6$, $Cl(OH)_7$, has no significance whatever, since the octet theory imposes a limit of four on the primary covalency of all the lighter elements. It is therefore very doubtful whether any of these acids, except silicic acid, can exist, unless as "molecular compounds" held together by residual electrovalencies, *i. e.* by stray fields from primary electrovalencies such as have been postulated in the formula for sulphuric acid. The place of the old "ortho-acids" is taken by the series of acids and ions which contain four oxygen atoms, as in

$$H_4SiO_4, \quad H_3PO_4, \quad H_2SO_4, \quad HClO_4,$$

and

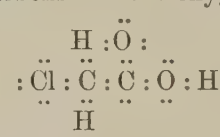
$$SiO_4''''', \quad PO_4''', \quad SO_4'', \quad ClO_4',$$

where the maximum covalency of four is reached; at the same time the maximum development of electrovalency makes these acids and ions more stable than those containing less oxygen.

4. *Acidifying Properties of Oxygen.*

The theory of intramolecular ionization leads to a novel explanation of those acidifying properties which led Lavoisier to bestow the name of oxygen upon this element. In general, acidity may be traced to the repulsion between a heavy positive nucleus and the light nucleus of a hydrogen atom; this results finally in the expulsion of the latter in the form of a detached proton or hydrogen ion, which leaves behind its electron in the form of a negative charge on the anion. The repulsive force increases progressively in the series $\equiv CH$, $=NH$, $-OH$, ClH, partly because of the increased weight of the nucleus, but apparently also in some inverse proportion to the number of hydrogen nuclei on which the repulsion acts.

This last effect appears to find an explanation in the observations of Rankine (Trans. Faraday Soc. xvii. p. 719, 1922) on the collision areas of the hydrides. These observations have shown that the size of the octet increases progressively from neon to methane, perhaps because of the mutual repulsion of the adherent hydrogen nuclei, but also as an obvious result of the weakened grip of the central nucleus on the surrounding electrons as protons are transferred from the inside to the outside of the shell. If these sizes are regarded as fixed, it is clear that the repulsive action of the nucleus in hydrogen fluoride as compared with that in methane may increase much more rapidly than its mass since Bohr has calculated that the electric field outside an octet would vary as the *tenth* power of the distance from the nucleus (see Langmuir, Trans. Faraday Soc. xvii. p. 609, 1922). This repulsion can apparently be transmitted through a series of atoms, since a relatively distant chlorine atom produces a marked increase of acidity in compounds such as the chloracetic acids, where the chlorine is separated from the hydrogen by a chain of two carbons and one oxygen, thus

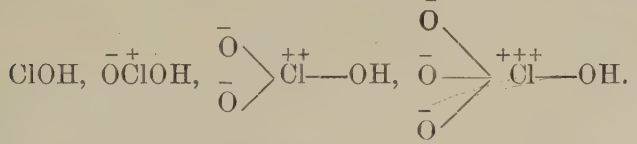


In all such cases the mechanism by which the repulsion is transmitted would appear to be a displacement of the nuclei relatively to the shells of electrons (compare Langmuir, Trans. Faraday Soc. xvii. p. 609, 1922), *e.g.* from left to right in the above formula, thus increasing the final repulsion of the nucleus of the hydroxylic oxygen for the terminal hydrogen nucleus which is split off as an ion. Whatever the mechanism may be, however, it is clear that the effect is cumulative for several halogens, but diminishes rapidly and progressively as the line of intervening atoms is lengthened.

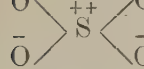
A more effective way of increasing the repulsion is, however, to add a positive charge to the repelling atom; and this can be done by bracketing it with an oxygen atom, as described in the preceding section, since under these conditions the oxygen atom always acquires a negative charge, whilst a positive charge is transferred to the atom which is bracketed by it. The effect of this is seen on comparing the neutrality of alcohol, $CH_3{-}{-}CH_2{-}{-}OH$, with the weak acidity of acetic acid, $CH_3{-}{-}\overset{+}{C}\!\!<\!\!\begin{matrix}\bar{O}\\ OH\end{matrix}$, where the positive

charge on the carbon atom transmits through the hydroxylic oxygen a repulsion just sufficient to enable the terminal hydrogen nucleus to escape as an ion. The direct effect of the carboxyl oxygen is probably small, since the repulsive action of its heavy nucleus is largely neutralized by the negative charge which it carries.

On the same basis the acid H—Cl—O or H—Cl=O would be stronger than hydrochloric acid; but in practice the hypothetical oxy-acid passes (as described above) into the more stable electrically-neutral molecule H—O—Cl, where the repulsive action of the chlorine is now required to operate through an oxygen atom, so that the compound is weaker than hydrochloric acid instead of stronger. When, however, the chlorine is now bracketed with additional oxygen atoms, each of these contributes an additional positive charge to the chlorine, and makes the acid not only more stable but also stronger in the series



This procedure is, however, limited to the introduction of four oxygen atoms, since the octet is unable to carry any larger number of nuclei.

The converse process of diminishing the acidity of a compound by imposing a negative charge on one of the repelling atoms is most familiar in the polybasic acids, such as sulphuric acid . In this case the splitting off of one hydrogen nucleus leaves behind a negative charge  , which *weakens* the repulsion transmitted from the nucleus of newly-ionized oxygen atoms through sulphur and oxygen to the second hydrogen nucleus, and so makes HSO_4' a weaker acid than H_2SO_4. In the same way the progressive diminution of acidity in the series $HClO_4$, H_2SO_4, H_3PO_4, H_4SiO_4 may be associated with the diminishing positive charge on the central atom of the ion, thus Cl^{+++}, S^{++}, P^{+}, Si, as well as with the diminishing mass of the nucleus.

5. *Influence of Intramolecular Ionization on Physical Properties.*

It will be noticed that in Sir Joseph Thomson's classification carbon dioxide and nitrous oxide both appear in Group I. as non-ionized molecules. It therefore remains to examine how far the views set out above are in harmony with the observed physical properties of these gases, and for this purpose the exact effect of the rearrangement of the nuclear charges on passing from one gas to the other must be considered. In the first place, it should be noticed that the repulsion between the nuclei of C and O will be very similar to that between N and N, since if these forces can be assumed to be governed still by the law of inverse squares, the repulsions would be in the ratio 48 : 49. In the second place, the view has been adopted that the nuclei are not rigidly fixed in the centre of the enveloping octets, but are able to adjust themselves to the attracting and repulsive forces acting upon them. Under these conditions it may be doubted whether any important stray field of force would escape beyond the cage of electrons in which all the nuclei are embedded. This conclusion is indeed almost inevitable in view of the fact that the similarity of the gases appears, not only in their refractive indices and specific inductive capacities, but also in the much wider range of physical properties tabulated by Langmuir. On the other hand, the stability and other chemical properties of the molecule which depend on fields of force *within* the molecule may be influenced very profoundly, on the lines discussed in the present paper, by these internal electrical forces.

6. *Summary.*

(1) Internal ionization is postulated in a number of compounds where the charges on the nuclei are not balanced by the enveloping electrons.

(2) Stability in oxy-acids depends on the presence of a positive charge on the central atom of the ion. This also increases the strength of the acid.

(3) A maximum of stability and of strength is reached in acids containing four atoms of oxygen round the central atom of the ion.

University Chemical Laboratory,
Cambridge.

CXVI. *Note on the Theory of the Specific Heat of Liquids.* *By* F. A. Lindemann *.

In the January number of the Philosophical Magazine Professor Honda has put forward a theory of the specific heat of liquids which can scarcely be allowed to pass unchallenged. It applies primarily to monatomic substances, and may briefly be outlined as follows :—The atoms in a solid execute translational vibrations according to the usual theory with the mean energy $3Rf(\theta_1/T)$, θ_1 being the characteristic temperature and $f(\theta_1/T)$ the function which according to the quantum theory determines the energy content. In addition to this, he assumes the atoms to carry out rotational oscillations about their centre of gravity in the solid, being constrained by the directive forces of the neighbouring atoms. Fusion he assumes to occur at the temperature at which the energy of these rotational vibrations becomes so large that the atoms execute continuous rotations. He neglects the work done against cohesion in the change of volume on fusion, and explains the latent heat of fusion as the energy which these new degrees of freedom of continuous rotation must acquire. Deviations from the atomic heat in the liquid proper to the three translational degrees of freedom plus two or three rotational degrees of freedom are explained by supposing that the potential energy in the translational oscillations may diminish if the atom executes long unconstrained free paths like the atoms in a gas.

Apart from the first generally accepted view of the translational vibrations, scarcely one of these assumptions is free from objection.

Atoms cannot rotate about their centres of gravity, as their moments of inertia are much too small. They are of the order Σmr^2, where m is the mass of one electron and r its mean distance from the nucleus, and are clearly less than 10^{-42}. Since $I\nu$ must be $4\pi^2 nh$, I being the moment of inertia, ν the frequency of rotation, n an integer, and h Planck's constant, therefore ν would have to be of the order 10^{17}, *i. e.* the characteristic temperature θ of the order $5 . 10^6$. It is evident that rotation at ordinary temperatures is impossible, on account of the factor $e^{-\theta/T}$. If the atoms could execute rotational oscillations the energy of the solid would be larger than $3Rf(\theta_1/T)$ by an amount $3Rf(\theta/T)$, θ being the characteristic temperature corresponding to the rotational frequency. On melting, if Prof. Honda's theory were true, these oscillations would become complete

* Communicated by the Author.

rotations and the potential energy would become free, *i. e.* a negative heat of fusion would result. If atomic rotations really occur in fluids, they must occur in a gas. If this were so, the atomic heat of mercury vapour would be 3R and the ratio of the specific heats 1·333... instead of the observed value of 1·67. The work done against cohesion by expansion on fusion is by no means negligible, as is assumed, but amounts to about half the latent heat. Finally, the atoms could only execute free paths without constraint if they were comparatively far apart. On fusion, their mean distance in general increases by little more than 1 per cent. If their amplitude of oscillation is 12 per cent. on fusion, therefore at most 1/13 of their paths could be executed under diminished constraint and hence no material diminution of the potential energy can take place.

For each and all of these reasons, Prof. Honda's theory must therefore be rejected. To avoid ambiguity, it may perhaps be worth while briefly to restate the theory which I had believed to be currently accepted.

Under the influence of their mutual attractions and repulsions the atoms in a solid form a space-lattice, regular in crystals, irregular in glasses. Their thermal energy at constant volume is in the form of translational oscillations, whose frequency is determined by the mass and the restoring force. A simple application of Taylor's theorem shows that the restoring force is elastic for small displacements, but does not remain so for large displacements. Hence the mean potential energy equals the mean kinetic energy at low temperatures, but may exceed it near the melting-point. At the melting-point some discontinuities in the atom collide or overlap, presumably orbits of peripheral electrons. Hence a crystal has a sharp melting-point, a glass an indefinite one. Monatomic solids expand on fusion, and about half the latent heat is simply work done against the cohesive forces. On account of the greater distance between the atoms in the liquid, the restoring force is less than in the solid and consequently the atoms' frequency and the characteristic temperature θ_2 must be lower. The balance of the latent heat is therefore probably accounted for by a term

$$3\mathrm{R}\int_0^{\mathrm{T}m}(f(\theta_1/\mathrm{T})-f(\theta_2/\mathrm{T}))d\mathrm{T}.$$

This point of view appears to account for the facts quite adequately and consistently, and unless Prof. Honda can show that it involves difficulties comparable to those inherent in his theory it would seem preferable to adhere to it.

CXVII. *The Total Reflexion of X-Rays.* *By* Arthur H. Compton, *Ph.D., Wayman Crow Professor of Physics, Washington University, Saint Louis* *.

1. *Deviations from Bragg's Law.*

THOUGH direct attempts to measure the index of refraction of different substances of X-rays have hitherto failed, deviations from Bragg's relation,

$$n\lambda = 2D \sin\theta,$$

have been observed which have been ascribed to an appreciable refraction of the X-rays as they enter the crystal. These deviations were first observed by Stenström †, using wave-lengths greater than 2·5 Å.U. Duane and Patterson ‡ and Siegbahn § have also noticed that even with ordinary X-rays the wave-lengths calculated from measurements in the different orders of reflexion do not exactly agree with each other. Stenström's conclusion that these experiments indicate appreciable refraction was criticized by Knipping ‖ ; but a more careful analysis by Ewald ¶ shows a quantitative agreement between the discrepancies observed by Stenström and those calculated on the refraction hypothesis.

The fact that Bragg's law cannot be strictly true seems to have been pointed out first by Darwin **, who gives for the difference between the observed glancing angle θ and the angle θ_0 anticipated from Bragg's formula,

$$\theta - \theta_0 = \delta / \sin\theta \cos\theta.$$

Here

$$\delta = 1 - \mu,$$

where μ is the index of refraction of the X-rays in the crystal. An expression which gives the index of refraction from measurements of the glancing angle for different orders of reflexion is

$$\delta = \frac{\lambda_1 - \lambda_2}{\lambda_2} \cdot \frac{n_2^2}{n_2^2 - n_1^2} \sin^2\theta_1, \quad . \quad . \quad . \quad . \quad (1)$$

where λ_1 and λ_2 are the apparent wave-lengths as measured

* Communicated by the Author.

† W. Stenström, Dissertation, Lund (1919).

‡ Duane and Patterson, *Phys. Rev.* xvi. p. 532 (1920).

§ M. Siegbahn, *Comptes Rendus*, clxxiii. p. 1350 (1921) ; pp. 174, 745 (1922).

‖ P. Knipping, *Zeits. f. Phys.* i. p. 40 (1920).

¶ P. P. Ewald, *Phys. Zeits.* xxi. p. 617 (1920).

** C. G. Darwin, Phil. Mag. xxvii. p. 318 (1914).

in the n_1 and n_2 orders respectively, and θ_1 is the glancing-angle for the n_1 order *. If the index of refraction of the crystal is known, the true wave-length can be calculated from the formula,

$$n\lambda = 2D \sin\theta\left(1-\frac{\delta}{\sin^2\theta}\right). \quad . \quad . \quad . \quad . \quad (2)$$

Duane and Patterson † find an apparent difference in the wave-length of the tungsten Lα line, $\lambda = 1{\cdot}473$ Å., as observed in the first and second order from calcite, of $\lambda_1 - \lambda_2 = 0{\cdot}00015$ Å. According to equation (1), this means an index of refraction *less* than unity by $\delta = 8 \times 10^{-6}$. Their similar measurements on 1·279 and 1·096 Å. give $\delta = 10$ and 3×10^{-6} respectively.

2. *Drude-Lorentz Theory of Dispersion.*

According to the Drude-Lorentz theory of dispersion ‡, the index of refraction of a medium for radiation of very high frequency is given approximately by

$$\delta = 1-\mu = \Sigma \frac{n_r e^2}{2\pi m(\nu^2 - \nu_r^2)}. \quad . \quad . \quad . \quad . \quad (3)$$

Here n_r represents the number of electrons per unit volume which vibrate with the natural frequency ν_r, e and m have their usual significance, ν is the frequency of the radiation, and the summation is taken over the different types r of the electrons. If, as in the case of ordinary X-rays traversing matter composed of light atoms, the frequency of the

* Darwin's investigation shows that, in spite of the fact that the wave-length is less than the distance between the individual atoms, refraction problems may be treated in the usual manner. If then θ and λ are the glancing angle and wave-length respectively outside the crystal, and θ' and λ' the corresponding angle and wave-length within the crystal,

$$\frac{\lambda}{\lambda'} = \mu; \quad \text{and} \quad \frac{\cos\theta}{\cos\theta'} = \mu, \quad \text{or} \quad \frac{\sin\theta'}{\sin\theta} = \frac{1}{\mu}\left(1-\frac{1-\mu}{\sin^2\theta}\right).$$

But Bragg has shown that

$$n\lambda' = 2D \sin\theta';$$

whence

$$n\lambda = 2D \sin\theta\left(\frac{1-\mu}{\sin^2\theta}\right),$$

which is equation (2). This gives the true wave-length in terms of the known grating space and the observed glancing angle. To determine the index of refraction, the glancing angles θ_1 and θ_2 for two different orders n_1 and n_2 must be measured. This gives two equations (2), from which the unknown wave-length λ may be eliminated, giving, after some reduction, equation (1).

† Duane and Patterson, *loc. cit.*

‡ *Cf., e. g.,* H. A. Lorentz, 'The Theory of Electrons,' 2nd ed. p. 149.

radiation is considerably higher than the natural frequency of the electrons, this becomes very nearly,

$$\delta = \frac{ne^2}{2\pi m\nu^2}, \quad \ldots \ldots \quad (4)$$

where n is the total number of electrons per unit volume of the medium.

If X-rays of wave-length 1·473 Å. traverse calcite, this expression (4) indicates an index of refraction which is less than unity by about 8×10^{-6}. For $\lambda=1{\cdot}279$, $\delta=6\times10^{-6}$, and for $\lambda=1{\cdot}096$, $\delta=4{\cdot}5\times10^{-6}$. The close correspondence between these theoretical values and the values calculated from Duane and Patterson's experiments can leave little doubt but that the consistent changes in apparent wave-length with order which they observe are due to refraction.

3. *Observation of Total Reflexion of X-rays.*

Since the refractive index is less than unity, a beam of X-rays striking a plane surface at a sufficiently large angle of incidence should be totally reflected. The critical glancing angle is given by

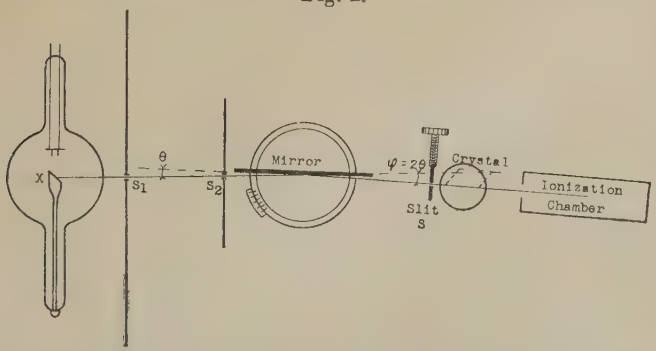
$$\cos\theta = \mu,$$

or

$$\sin\theta = \sqrt{2\delta}.$$

For 1·279 Å., the value of δ for crown glass of density 2·52 is given by equation (4) as $5{\cdot}2\times10^{-6}$, in which case $2\theta=22$ minutes of arc, which is a readily measurable deflexion *.

Fig. 1.



In searching for the totally reflected beam, the apparatus was set up as shown diagrammatically in fig. 1. The beam of X-rays passing through the slits S_1 and S_2 had an effective

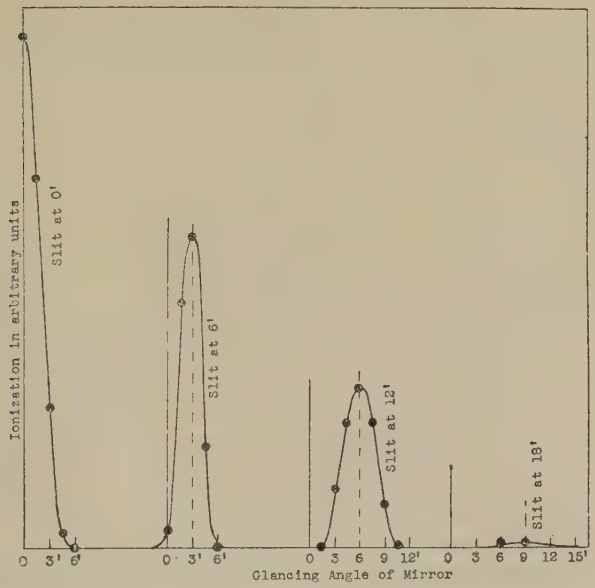
* In this calculation, the composition of crown glass was assumed to be $CaO\,.\,Na_2O\,.\,2SiO_2$. However, for a given density, variations in the composition affect only very slightly the index of refraction as calculated from equation (4).

width of about 2 minutes of arc. The mirror was a piece of ordinary plate glass, of density 2·52, mounted upon the prism table of a spectrometer. The vernier of the spectrometer was used only to check the accuracy of a lamp and scale system, which was set at such a distance from the mirror that a rotation of the mirror through an angle of $\theta = 1$ minute gave a deflexion of 1 mm. The slit S could be moved by a micrometer screw through any desired angle ϕ, while the opening into the ionization chamber was wide enough to admit rays coming from the mirror through a range of about 1·5 degrees.

The zero position of the slit S was determined by removing the mirror and adjusting the slit S for maximum deflexion. The zero position of the mirror could not be determined by the maximum deflexion, since, as we shall see, the beam reflected from the surface is nearly as intense as the primary, so that the maximum deflexion is not given when the front surface of the mirror just bisects the primary ray, but when part of the primary ray is reflected from its front surface. A more satisfactory method of determining the mirror's zero point was to turn it until the visual image of the slit S_1 coincided with the real slit.

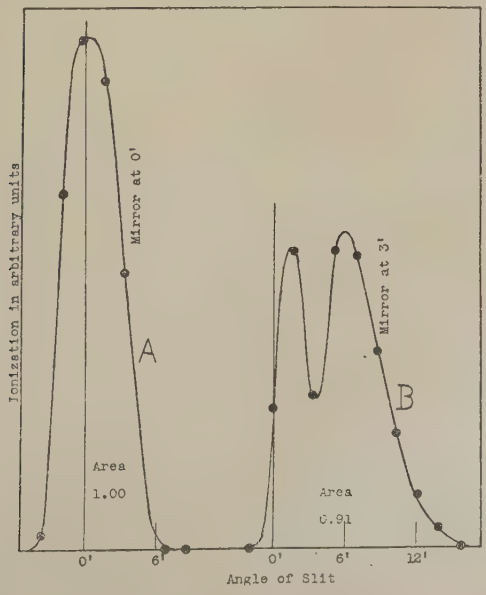
In searching for the predicted total reflexion, the slit S was moved several minutes of arc from the zero position, and the ionization current noted for various positions of the mirror. The results thus obtained, for different positions of the movable slit, are shown in fig. 2. For example, when the slit was at an angle $\phi = 12'$, on turning the mirror from zero to $12'$ the intensity of the X-rays entering the chamber increased from zero at small angles to a maximum at $6'$ and then fell to zero at larger angles. If the X-rays entering the chamber were diffusely scattered, they should have been of maximum intensity when the mirror was at the smallest glancing angle at which all the primary beam would impinge upon its front surface, *i. e.* at about $4'$. Thus the fact that the X-rays are in every case of maximum intensity when the angle $\phi = 2\theta$ shows that there is an approximately specular reflexion of the X-rays at these small angles. The increasing breadth of the reflected beam at the larger angles shows that the reflexion is not perfectly regular. It appears rather that the glass surface reflects the X-rays in much the same manner that the air above a heated street reflects light to form a mirage. The fact that no appreciable reflexion is observed at angles as great as $\phi = 18'$ means that for the greater part of the X-ray beam the critical glancing angle θ is less than $9'$.

Fig. 2.



The maximum intensity occurring when the glancing angle of the mirror is half that of the slit indicates specular reflexion.

Fig. 3.



The reflected energy is nearly equal to the incident energy, indicating total reflexion.

If the observed phenomenon is really one of total reflexion, the energy in the reflected beam should be nearly as great as that in the primary beam. A measure of the total energy in each beam was obtained by integrating the observed ionization as the slit S was moved across the beam. Curve A of fig. 3 was thus obtained when the mirror was set at zero, and curve B when at 3′. This small glancing angle was necessary in order not to exceed the critical angle for the shorter wave-lengths. In order to satisfy this condition with greater certainty, the tube was operated at the comparatively low potential of about 12,000 peak volts. But the angle was so small that part of the primary beam was not intercepted by the mirror, giving rise to a sharp peak at 1′·5 in curve B. The ratio of the areas of the two curves, 0·91, shows that the greater part of the incident energy is indeed reflected.

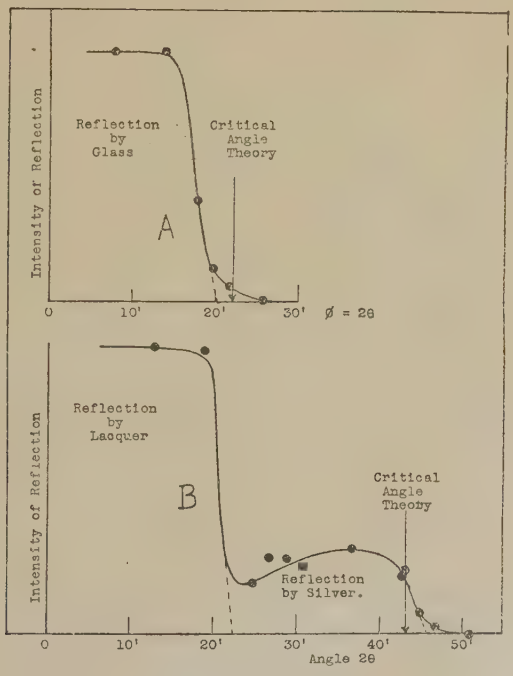
4. *The Index of Refraction for X-rays.*

In order to test quantitatively the theoretical dispersion formula for these very high frequencies, it was necessary to determine the critical glancing angle for a known wave-length. For this purpose the calcite crystal C, on the crystal table of a Bragg spectrometer, was placed in the path of the reflected beam, so that its spectrum could be studied. The procedure then consisted in measuring the intensity of a given spectrum line in the beam reflected from the mirror, and in finding the angle $\phi = 2\theta$ beyond which the line fails to appear. The results of these experiments are shown in fig. 4. Curve A shows the intensity of the reflexion of the tungsten L line $\lambda = 1{\cdot}279$ Å. by the plate-glass mirror at various angles $\phi = 2\theta$. It will be seen that the line has almost disappeared from the reflected beam at a critical glancing angle of about 20′. Curve B shows the intensity of the same line as reflected from the surface of a silvered glass mirror coated with a thin film of lacquer. It is apparent that the critical angle for the lacquer is passed at about 22′, while the line finally disappears not far from the angle 43′ predicted by Lorentz's theory as the critical glancing angle for silver. From these curves we may take the critical glancing angle for glass as $\theta = \phi/2 =$ about 10′, for lacquer as about 11′, and for silver as about 22′·5. These values correspond to indices of refraction less than unity by $4{\cdot}2 \times 10^{-6}$ in the case of glass, $5{\cdot}1 \times 10^{-6}$ in the case of lacquer, and $21{\cdot}5 \times 10^{-6}$ in the case of silver.

The spectrum of the rays reflected from glass at the angle

$\phi = 8'$ is shown in fig. 5, curve A, as compared with the spectrum of the primary beam, curve B. The ordinates of the spectrum of the reflected rays are magnified by a factor of 3. It will be noticed that whereas the spectrum of the primary rays begins at $\theta = 2°{\cdot}1$, corresponding to a wave-length of 0·22 Å., the spectrum of the reflected rays begins rather gradually at about $4°{\cdot}5$, and apparently, if the slits

Fig. 4.



Total reflexion and critical angles for $\lambda = 1{\cdot}279$ Å.

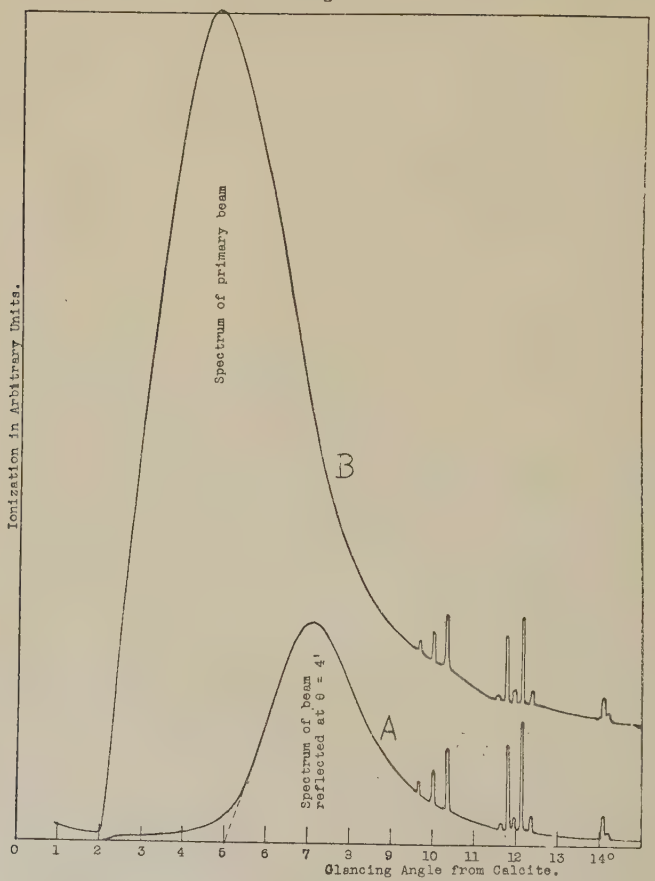
were sufficiently narrow, would begin at about $5°{\cdot}0$. Thus $\phi/2 = 4'$ is the critical angle for a wave-length of about ·52 Å., corresponding to a value of $1 - \mu = 0{\cdot}9 \times 10^{-6}$. This value is not, however, as reliable as the values obtained from the spectrum line.

5. *Comparison of the Experiments with Theory.*

The calculation of the index of refraction of crown glass is not difficult, since the frequency of the radiation employed is considerably higher than that of the K absorption

band of the heaviest element, calcium, in the glass. Consequently, the simple formula (4) can be applied with very little error. In the case of silver, however, the wave-length employed, 1·279 Å., is intermediate between the critical K and L absorption frequencies. It is thus necessary to take into account the natural frequencies of the electrons in both

Fig. 5.


Ionization in Arbitrary Units.
Spectrum of primary beam
B
A
Spectrum of beam reflected at θ = 4'
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14°
Glancing Angle from Calcite.

of the inner rings. It is surprising, however, how small a difference the corresponding degree of resonance makes. Thus if the middle of the K absorption band is taken as ·39 Å., that of the L series as 2·9 Å., the number of electrons in the K ring as 2, and in the L ring as 8, the value of δ, according to equation (3), is $19{\cdot}8\times10^{-6}$; but the approximate equation (2) gives the corresponding value as $20{\cdot}3\times10^{-6}$, a difference of only 2 per cent.

In Table I. are given the results of the experimental measurements of the index of refraction as compared with the theoretical values for glass, silver, and lacquer.

TABLE I.

Substance.	Density.	Wave-length Å. U.	Critical angle θ, expt.	$\delta=1-\mu$, experiment.	$\delta=1-\mu$, theory.
Glass.....	2·52	1·279	10′	$4{\cdot}2\times10^{-6}$	$5{\cdot}2\times10^{-6}$
Glass.....	2·52	·52	4′	$0{\cdot}9\times10^{-6}$	$0{\cdot}7\times10^{-6}$
Silver ...	10·5	1·279	22′·5	$21{\cdot}5\times10^{-6}$	$19{\cdot}8\times10^{-6}$
Lacquer..	—	1·279	11′·0	$5{\cdot}1\times10^{-6}$	—

It is at first sight surprising that the value of δ should be greater for lacquer than for glass. Some recent experiments by Miss Laird have indicated *, however, that the density of thin films of celluloid increases considerably as the films become very thin, rising from the value of 1·41 for thick films to greater than 2·5 for the thinnest films measured. In view of the hydrogen content of these organic substances, it thus appears that the electron density in these dense thin films is greater than in glass. Thus in every case the experimental values of the index of refraction are in satisfactory accord with the usual electron theory of dispersion †.

6. *Application to Physical Problems.*

This establishment of the theoretical dispersion formula makes it possible to calculate with accuracy the index of refraction for these very high frequencies by substances containing only the lighter atoms. There remains some uncertainty with regard to the natural frequencies of the K and L electrons in the heavier elements; but as we have seen in the case of silver, errors from this cause can hardly be serious. Fortunately, the crystals most used in X-ray spectroscopy are composed of relatively light elements. In the case of calcite, formula (4) gives the value of $1-\mu$ as $3{\cdot}67\lambda^2\times10^{-6}$, where λ is expressed in Ångström units. As compared with formula (3), this expression is accurate to 1 per cent. for wave-lengths less than 2 Å., and is accordingly reliable for corrections of the wave-length throughout the usual X-ray spectrum. The corresponding expression for

* E. R. Laird, Phys. Rev. xix. p. 384 (1922).

† There is an apparent tendency for the experimental value of $1-\mu$ for glass to fall below its theoretical value, though the difference is hardly more than the experimental error. If the difference is real, it may indicate the existence of a thin layer of matter of low density, such as water or oxygen, on the surface of the glass.

rock-salt is $3{\cdot}04\lambda^2 \times 10^{-6}$, which should also be accurate to 1 per cent. over the same range. Using these values for the index of refraction, the true wave-length can be calculated from the glancing angle according to equation (2).

A matter of considerable interest is the prominence of the L series spectrum lines in the spectrum of the totally reflected rays.. In the primary beam, operating the tube at about 70,000 peak volts and using a wide opening into the ionization chamber, the continuous background is more prominent than even the strongest of the L series lines. But when wave-lengths shorter than 0·5 Å. are absent, as they are in the reflected beam, the spectrum lines stand out much more prominently. In fact, the continuous background has almost disappeared. It is obvious from this result that the principal part of the continuous background in this region consists of the higher orders of reflexion of the shorter wave-lengths, and that comparatively little energy of wave-lengths greater than 1 Å. occurs in the general radiation.

This experiment illustrates the use of the phenomenon of total reflexion as a means of filtering the *short* wave-lengths from a beam of X-rays, a result which cannot be secured by absorption filters. Unfortunately the method can be applied only in the case of very narrow beams of X-rays, having a breadth of the order of a few minutes of arc. But in the case of such beams, the reflexion is so nearly total that the reduction in intensity is not great, while the critical glancing angle is so well defined that the shorter wave-lengths are rather sharply cut off. For use as such a filter, a mirror with a platinum surface is to be recommended, because its index of refraction differs so greatly from unity that the critical angles are comparatively large.

The existence of an index of refraction of the magnitude predicted by the classical electron theory would seem irreconcilable with the view that one quantum of X-rays can affect but a single electron. For there would seem to be no possibility of refraction unless the ray can spend a part of its energy in setting in vibration some of the electrons over which it passes so as to give rise to a secondary ray which will combine with the primary train. But this involves the idea that parts of the quantum are capable of affecting the traversed electrons. It is not easy to reconcile this result with such experiments as that of the softening of scattered X-rays *, which seem to demand that each electron affected by the primary rays receives both the momentum and the energy of a whole quantum.

* *Cf.* A. H. Compton, Bulletin Nat. Research Council, No. 20, p. 16 (1922).

It is of value to note that equation (4) supplies a means of determining with fair accuracy the wave-length of an X-ray beam from an experimental measurement of its index of refraction, if the number of electrons per unit volume is known. If the number of effective electrons per atom is taken equal to the atomic number, as X-ray scattering experiments show is at least approximately the case, the measured value $\lambda = 4{\cdot}2 \times 10^{-6}$ for glass means a wave-length of 1·18 Å. This value is independent of any knowledge of crystalline structure or of the energy quantum, and so gives a very valuable confirmation of the wave-length 1·28 Å. calculated on the basis of other more accurate though less fundamental methods.

Perhaps of greater importance is the fact that, knowing the wave-length, it is possible to calculate from the observed index of refraction the number of electrons per atom which are affected by the incident X-rays. In calculating the theoretical value of the index of refraction from formula (3), the number of electrons per atom has been taken equal to the atomic number. From the accuracy with which the index as thus calculated agrees with the experiments, it follows that this assumption is probably correct to within about 5 per cent.

The two most direct methods hitherto employed for determining the number of electrons in the outer part of the atom are the study of the scattering of alpha rays by atomic nuclei and the measurement of the intensity of scattered X-rays. The first method determines the charge on the atomic nucleus, and it is not certain *à priori* that the charge thus measured is identical with the charge on the electrons which are responsible for high frequency radiation. The intensity of the scattered X-rays, on the other hand, though determined by the electrons exterior to the nucleus, is a function not only of their number but also of their arrangement and size. The index of refraction is theoretically independent of the arrangement and size of the electrons, and depends upon their resonance only to the same extent as does the scattering. Thus an estimate of the number of mobile electrons in an atom based upon a measurement of the index of refraction is more reliable than a similar estimate based upon these other methods. It is accordingly gratifying that such a measurement confirms the result of the earlier work, indicating that the number of electrons per atom which are affected by high frequency radiations is equal to the atomic number.

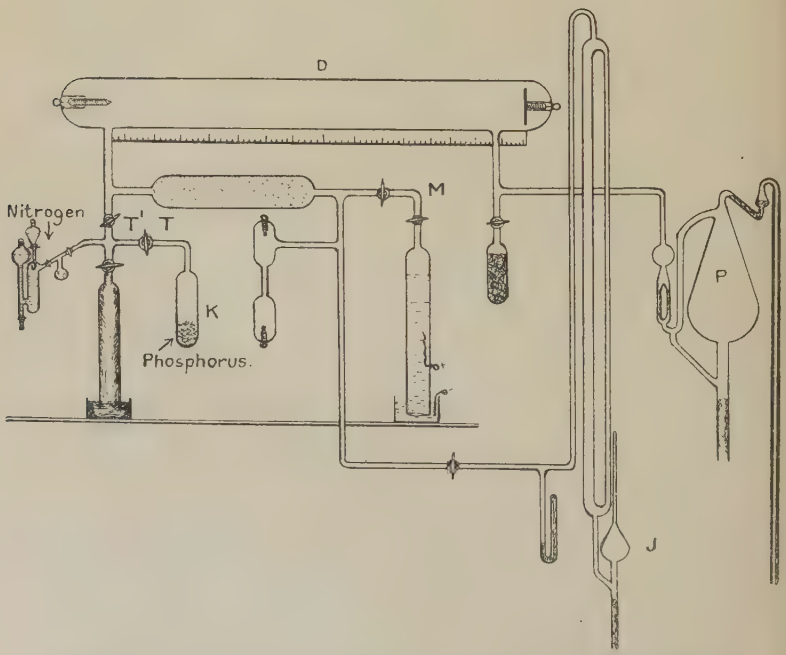
Washington University,
St. Louis,
Dec. 6, 1922.

CXVIII. *Luminous Pulsations in the Glow of Phosphorus.*

By H. P. Waran, *M.A., Ph.D.* (*Cantab.*), *F.Inst.P.**

LORD RAYLEIGH has recently called attention † to the remarkable travelling pulses of luminosity observed when oxygen comes into contact with phosphorus vapour. Following the earlier procedure of Joubert he has examined the travelling pulses of luminosity, using the method of allowing atmospheric air (containing oxygen) to leak slowly into a space in which phosphorus vapour is being continually produced by a lump of phosphorus. About two years ago I happened to observe the phenomenon of the periodic luminosity of phosphorus in somewhat different circumstances, with an apparatus of the form shown in fig. 1, which was

Fig. 1.



being used for quite a different purpose. Since my observations differ in some respects from those of Lord Rayleigh in the paper referred to, it may be of some interest if I set out the facts of my observation in some detail.

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S., F.Inst.P.
† Proc. Roy. Soc. A. xc. p. 372 (1921).

In the apparatus of fig. 1, K is the side tube containing a little phosphorus used to free the apparatus from traces of oxygen; while M is the arrangement by which a small bubble of electrolytic oxygen could be introduced into the system whenever required. D is a large discharge-tube over 50 centimetres in length and about 4 centimetres in diameter, and connected to it are the Töpler pump P and McLeod gauge J. The taps T and T′ having been kept open for some time, the whole of the apparatus became fouled by the phosphorus vapour and the thin deposit of phosphorus all over the glass surface could be readily seen by the change in tint throughout. Experimenting under conditions of total darkness in the room, when a bubble of oxygen was let into the apparatus the short flash of luminosity throughout the apparatus was followed by bright and practically momentary flashes of luminosity in the wider portions of the pump P and the McLeod gauge J. The perfectly dark and comparatively long intervals between the flashes of luminosity were of the order of about twenty seconds to start with. This period diminished gradually until, after about twenty to thirty flashes, the luminosity was faint and the pulsations, if any, too difficult to be followed with certainty.

It was interesting to note that the smaller bulb of the McLeod gauge showed a shorter period and a lesser number of flashes and these flashes were quite out of phase with those occurring in the bigger bulb of the mercury pump. No flashes except the initial one on the first entry of oxygen were noticed in the large discharge-tube D.

The bulbs of the pump and gauge are connected to the rest of the apparatus by comparatively long and narrow tubing. Through these there was the possibility of a kind of damped oscillation of the gas between these bulbs and the large volume of the discharge-tube, maintained by the periodic explosions occurring at these bulbs at the far end. But difficulties were encountered in pursuing this line of explanation further. Though the circumstances of the travelling pulses of luminosity discussed by Lord Rayleigh and those of the periodic luminosity observed by the author are different, it is possible that the explanation for both is based on the same primary cause.

Though I had set aside this interesting observation for investigation at a more convenient opportunity, recently, since the publication of Lord Rayleigh's paper, I have tried to experiment further on the phenomenon with a view to explain some of the differences in our observations. The first difference noted by me was that whereas Lord Rayleigh

asserts the need for the presence of water vapour to maintain the travelling pulses of luminosity, oxygen dried over phosphorus pentoxide at a low pressure seems to be quite effective for producing the periodic flashes. Secondly, in my arrangement the whole of the oxygen is let in into the highly exhausted volume of the apparatus and is not gradually supplied by a process of leakage through a fine capillary tube. In these two respects amongst others the phenomenon of the periodic flashes seems to differ from the case of the travelling pulses of luminosity. It is also difficult to follow up the explanation of a travelling pulse from the circumference to the centre or *vice versa*, since on this view it is difficult to explain the further flashes after the first one has consumed all the available oxygen. It may be that by a process of damped oscillation between parts of the apparatus, or by a very slow flow of gas through the long and narrow connecting tubes, fresh supply of gas is continually available for the maintenance of the successive flashes.

To test these two possibilities further, two forms of apparatus as shown in figs. 2 and 3 were made. In fig. 2, pure dry electrolytic oxygen is stored at a low pressure in the bulb *b* over a layer of phosphorus pentoxide. The phosphorus is contained in a tube *t* immediately below the flash bulb B, and a stop-cock S separates these two volumes. Oxygen from *b* can be let into B by turning the half-filled stop-cock T, and the bubble of gas thus let in has to traverse the spiral of glass tubing before it enters the flash bulb. Because of this arrangement there is no large idle volume connected to the bulb B to permit of the oscillations of gas between the flash bulb and itself. This part of the apparatus is completely exhausted, and by opening the stop-cock S and warming the tube *t* phosphorus can be distilled over into B, where it deposits itself as a thin layer over the glass walls. This form of apparatus has the great convenience that it is complete in itself for the flash experiment. The admission of pure oxygen makes the products of combustion in the flash bulb practically disappear, leaving the vacuum in B as perfect as before, thus permitting the apparatus to be used again for observing another set of flashes. Experimenting with this apparatus, for every bubble of oxygen admitted into the apparatus a regular series of flashes was observed as expected, even after the oxygen had been dried by standing in contact with phosphorus pentoxide for over one and a half years. This proved two points. Firstly that the presence of water vapour is not essential for the maintenance of these series of periodic flashes, though it may be

necessary for the travelling pulses of luminosity. Secondly, that the flashes are not being maintained by a periodic supply of gas arising from the oscillations of gas between parts of the apparatus, with narrow connexions between them. This latter point is further supported by the observations with the similar apparatus of fig. 3, where the long spiral connecting tube is also dispensed with. To keep the large volume of the flash bulb quite dry and free from any

Fig. 2.

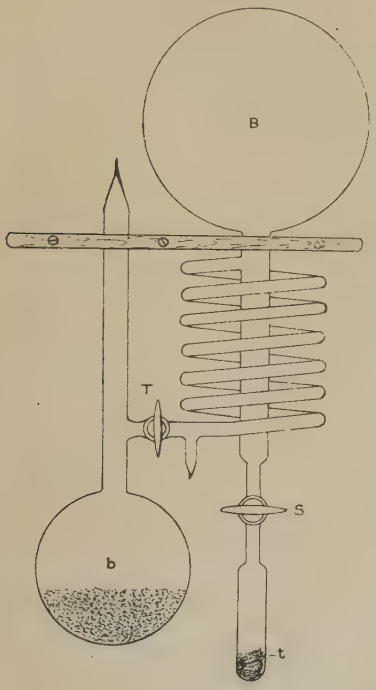
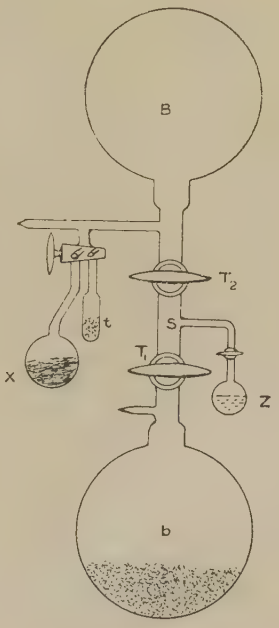


Fig. 3.



moisture introduced with the phosphorus distilled into it, a small bulb X of phosphorus pentoxide is permanently sealed on to it. A side tube leading to a bulb Z containing a little water enables water vapour to be added on to the bubble of oxygen let into the space S by turning the half-filled tap T_1 before the mixture of the two is let into the flash bulb by opening T_2. From the experiments with this apparatus it would appear that the influence of water vapour is not anything serious, and the effect, if any, is a slightly increased luminosity in the flashes.

Experimenting with this apparatus the sequence of

changes noted as characteristic of these flashes were as follows:—

(1) An initial luminosity for a brief interval on the admission of the bubble of gas into the system.
(2) Its quick decay to complete darkness.
(3) The origin of the periodic flashes.
(4) Their continued occurrence with gradually decreasing period.
(5) The disappearance of the final faint glow.

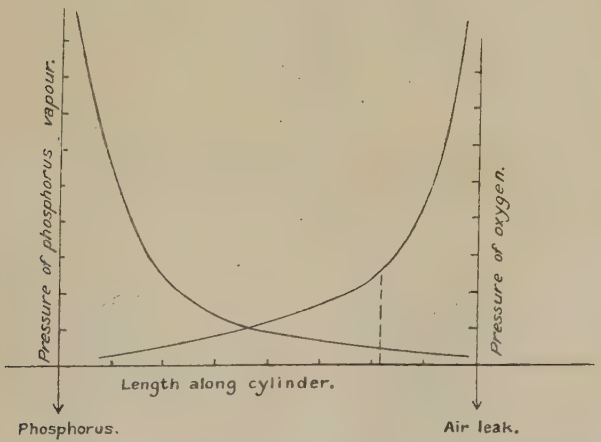
Any proper explanation of this phenomenon must be capable of satisfactorily accounting for this sequence of changes. Though the nuclear theory of Lord Rayleigh is satisfactory enough in explaining the propagation of the travelling pulses of luminosity studied by him, it does not seem to be applicable to the present case. The earlier conclusion of Joubert that below certain pressures too small to measure phosphorus would not combine with oxygen, seems to be suggestive of a profitable line of attack if we make the further assumption that the explosive or luminous combination of phosphorus vapour and oxygen is governed by the fact that, as in any explosive mixture, their partial pressure in the mixed atmosphere must bear a certain minimum ratio before combustion can spontaneously originate or be maintained in the mixture.

The validity of this assumption is proved by Lord Rayleigh's experiments on the travelling pulses of luminosity, where the luminous combination starts always at a particular level when oxygen slowly leaks into a system where a gradient in the vapour pressure of the phosphorus located at the other end exists. The situation is represented more clearly by the graphs of fig. 4, where the partial pressures of the constituents are plotted against the length of the cylinder. The change with time corresponds roughly to a vertical displacement of the partial pressure curves at different rates, and the propagation of a pulse of luminosity may be guided purely by the progressive change in this ratio at different levels along the tube. This is dependent on the rates at which oxygen and the vapour of phosphorus are flowing into each other from either end.

This line of explanation seems to suit the periodic flashes as well. For the conditions represented by the graphs of fig. 4 are exactly reproduced in the flash bulbs of the apparatus shown in figs. 2 and 3. To begin with, the inner surface of the flash bulb has a thin coating of phosphorus which is giving off inwards a slow stream of phosphorus

vapour, and there is a gradient of this pressure from the wall towards the centre when the flashes originate. The vapour of phosphorus, saturating the bulb to begin with, gets consumed by the first rush of oxygen, and this explains the initial glow. The bulb is now mainly filled with oxygen and particles of the oxide of phosphorus. The steady diffusion of phosphorus vapour into this central region of oxygen sets up in the course of a few seconds a circumferential zone of narrow width where the pressure of the phosphorus vapour is steadily increasing. As soon as it reaches the critical ratio combination results in this layer, which is seen as the first flash. This creates a situation quite favourable for the maintenance of the successive

Fig. 4.



flashes. The first flash leaves an inactive spherical zone of narrow width filled with particles of the oxides of phosphorus, and oxygen and phosphorus vapour diffuse into it from either side of it. A second flash follows when the critical ratio is reached again, and this action goes on producing the successive flashes, until the whole of the oxygen is used up. Since the pressure of oxygen falls with every flash, because of its expansion, the quantity of phosphorus vapour required to give the critical ratio decreases, and for a steady rate of evaporation of phosphorus from the walls the required vapour is formed in a shorter time and that accounts partially for the progressive diminution in the period of the successive flashes. The period suffers also a diminution because of the uncombined phosphorus vapour remaining in the region beyond the zone of active or luminous combination.

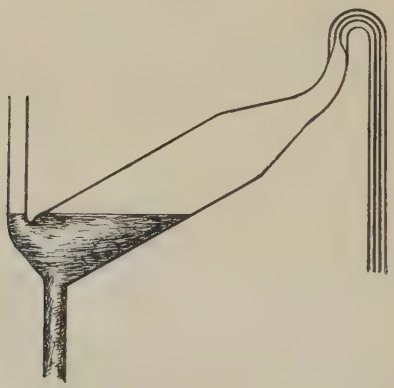
The correctness of this line of explanation can be checked by the following consequences of the explanation :—

(1) For a uniform intensity of illumination throughout this spherical layer of combination, when the bulb is viewed from the side it should show a greater intensity towards the circumference.

(2) The flashes of luminosity should not occur in the initial stages of the apparatus when there is only a little phosphorus vapour in the bulb and a layer of phosphorus has not been deposited on the walls. These are observed to be the case in practice.

Apart from these high frequency flashes with periods less than about 10 to 20 seconds there is an interesting type of long period flashes, often noticed with apparatus of large volume exhausted down to a very low pressure. A typical case of this is provided by the Töpler pump of the shape shown

Fig. 5.



in fig. 5, used to exhaust these flash apparatus. Its walls get contaminated with the phosphorus in course of time. If the apparatus connected to it contains a residual trace of low pressure oxygen and the Töpler pump be given a stroke and its cylindrical bulb watched with patience in total darkness, faint flashes with a period of the order of ten to fifteen minutes are often noticed. These flashes do not appear as instantaneous, but seem to be taking place during a definite interval of the order of a second or two during which a gradual growth and then a decay of the luminosity can be distinctly noticed. Their period also remains practically constant.

These long period flashes seem to be maintained by the slow feed of gas through the long and narrow connecting

tubes, at these very low pressures. To begin with, after the stroke of the pump, as the mercury level goes down in the pump forming the Torricellian vacuum above it, the space above gets saturated with the vapour of phosphorus evaporating from the walls. On the mercury level descending past the side tube the low pressure oxygen begins to flow in, and it takes some time before the critical ratio for the firing mixture is established, and hence the long period flash. This flash consumes the whole of the available supply of oxygen and necessitates a fresh supply flowing in for the second flash. If we raise the level of mercury at this stage and prevent the oxygen flowing into the bulb, the expected flash does not take place. This proves that it is the slow feed of gas that is responsible for the maintenance of the flashes in this case. Further, if by a few more strokes we reduce the pressure of oxygen, it ought to increase the period of the flash. This is found to be the case in practice, affording additional evidence in support of this explanation.

In conclusion, I must express my indebtedness to Prof. A. W. Porter, D.Sc., F.R.S., for his sympathetic interest in this work done at his laboratory.

University College, London.

CXIX. *The Mechanism of the Electric Arc. By* W. G. Duffield, *D.Sc., Professor of Physics in University College, Reading* *.

I HAVE been greatly interested in the recent discussions in the pages of the Philosophical Magazine of the theory which I ventured to put forward in 1919 to explain the repulsion experienced by the poles of the electric arc. I hope that at this stage a few remarks from myself may not be considered out of place †.

* Communicated by the Author.

† References :—

(1) Duffield, B. A. Report, Australia, 1914.
(2) Sellerio, *Nuovo Cimento*, xi. p. 67 (1916). The present writer regrets that he has not seen this paper.
(3) Duffield, Burnham, and Davis, Phil. Trans. Roy. Soc. A. 220. p. 109 (1919).
(4) Duffield, Burnham, and Davis, Proc. Roy. Soc. A. 97. p. 326 (1920).
(5) Ratner, Phil. Mag. xl. p. 511 (1920).
(6) Tyndall, Phil. Mag. xl. p. 780 (1920).
(7) Beer and Tyndall, Phil. Mag. xlii. p. 756 (1921).
(8) Tyndall, Phil. Mag. xlii. p. 972 (1921).
(9) Sellerio, Phil. Mag. xliv. p. 765 (1922).

I should like in the first instance to express my appreciation of the courteous way in which Professor Sellerio[9] has drawn my attention to his own work on this subject[2], published in 1916. I have little doubt that the cause which led me to ignore his 1916 paper was the same as that which led him to overlook the fact that in 1914 I had presented a communication[1] to the British Association, entitled "The Pressure upon the Poles of a Carbon Arc" (B. A. Report, Australia, 1914). I willingly forgive him the omission of any reference to a paper published in title only, but which I think it useful to mention, as it may serve to date the first observation of this phenomenon. I am the less uneasy regarding my own oversight, because in his 1916 paper Prof. Sellerio neglected to take into account, as he very frankly admits in his 1922 paper, the forces occasioned by the magnetic field of the earth and the rest of the circuit, the elimination of which were essential before the existence of any repulsive effect could be established.

I wish also to express to Prof. Sellerio my thanks for his appreciative comments upon the accuracy of the experimental work of my fellow-workers and myself upon this effect; but at the same time I wish that he had not been content to accept our figures for the corrections for the electromagnetic effect of the rest of the circuit, and to apply them to his own observations. I can scarcely believe that the dispositions of our two sets of apparatus were sufficiently alike to justify this. I had hoped that completely independent work might settle beyond dispute whether the variation of the force with the current is truly linear or not. I confess also that I find it difficult to accept the great difference between the anode and cathode pressures calculated by Prof. Sellerio, varying from a 12 to 1 ratio to a 2 to 1 ratio. We should expect action and reaction upon the two poles to be more nearly equal, because the only way in which momentum disappears from the arc-gap is through the agency of convection currents, and these we do not find to constitute a large proportion of the whole effect. According to the experiments of Burnham, Davis, and myself, the reactions upon anode and cathode are more nearly equal—indeed, in the case most carefully considered (the 6 mm. 10 amp. arc), the mean reactions only differ by 4 per cent., an agreement which is probably accidental. We do not find any evidence of "knees" in the curves connecting current and reaction, described by Prof. Sellerio[9]; our graphs were all smooth, though we repeated our observations with several different dispositions of the apparatus.

The Origin of the Forces upon the Poles.

In this connexion my remarks will be confined to three headings :—

(1) *The motion of ions under the electric forces in the arc.*

In a previous paper I put forward the view that the pressure upon the poles of an arc is not to be explained by the motion of ions arising solely from the electric field within it, or, to put it more generally, that the action of the electric field upon either pole of an arc balances the reaction upon it due to its bombardment by ions whose motion the electric forces occasion. We can, for example, easily show (*loc. cit.*[4]) that for an ion starting from rest with charge e in a uniform field of strength R, the rate of change in the momentum delivered to the pole of opposite sign is equal to Re, which is also the electric pull upon that pole.

This rule I believe to be one of the salient features of the arc, possibly a more remarkable feature than the existence of a small pressure upon the poles ; the precision with which it is obeyed may not be obvious, but it becomes apparent if we calculate upon any reasonable hypothesis the rate at which ions falling into a pole of opposite sign deliver momentum to it. If, for example, we suppose that positively-charged oxygen atoms, each carrying a charge $2e$, fall into the cathode in sufficient numbers to carry a current of 10/2 amperes in a 10 ampere arc, then, since they possess velocities induced by the potential drop just outside the pole, 11·6 volts (Duddell), that pole should experience, if there were no compensating action, a force which can easily be calculated to be of the order of seven hundred dynes. But experiment shows that the force only amounts to about 2 dynes; consequently, on the most unfavourable view, the compensation must be nearly complete, and the rule is obeyed with an accuracy of 0·3 per cent.

But the question has arisen whether the two dynes pressure results from an imperfection in the compensating mechanism, or from the impact of particles whose motion arises from some cause other than the electrostatic forces. I favour the latter, and have suggested that the outstanding pressure results from the *projection* of high-speed electrons from the cathode, whose momentum is transmitted through the body of the arc to the anode. Professor Tyndall[8] has discussed the balance theory from a point of view different from that which I originally put forward, and has come to the conclusion that it should hold good for an arc between poles large compared with the arc-gap and in which the ions move

viscously, but believes that in an actual arc the lack of symmetry occasions a departure from a true balance and can account for the observed reaction.

According to him the dissymmetry may be of two types—a dissymetry in the shape of the electrodes, such as may arise from the cathode becoming pointed, or a dissymetry due to the acceleration of the ions under the electric field. On these grounds he disputes my theory. I do not think his objections to complete compensation well-founded; though I am not sure that I am in a position definitely to disprove his contention, the following considerations appear to me to carry weight:—

(*a*) If in an arc with pointed electrodes any particles carrying charges fail to strike one of the poles, the latter is deprived of the momentum which their impacts would have occasioned; the pressure upon the pole is either reduced or unaffected according to whether the charges have, or have not contributed to the attraction acting upon that pole. I do not think the pressure could be *increased* by their removal.

Moreover, Professor Tyndall's reservation concerning the pointed cathode seems unnecessary, because he deduces from an experiment with an arc with a pointed electrode, which he enclosed in a quartz tube in order to eliminate convection currents, that the lateral loss of momentum is negligible.

(*b*) As evidence of a lack of balance with a pointed electrode, the case of the electric windmill has been cited. But the two types of discharge have very little in common. The apparent repulsion of a pointed conductor at a high potential is due to the pull of the Faraday tubes on the end of the conductor away from the point (Chattock, Phil. Mag. Aug. 1910). In an arc there are no free charges on the rear of the pole, so the Faraday tubes are concentrated in the space between it and the opposite electrode. It is worth noting that even with a high potential discharge we obtain an accurate balance if we arrange to concentrate the tubes of force on the pointed side of the electrode. I tried the following experiment:—A pointed rod, delicately pivoted, was connected to the negative pole of a not very powerful Wimshurst machine, and a plate, about 5 cm. in diameter connected to the positive terminal was brought near it. When the plate was within 2 or 3 cm. of the point the latter was on the whole stationary (though small fluctuations were observed; sometimes a very faint repulsion, occasionally a rather stronger attraction, due either to air-currents or to fluctuations in the working of the machine). Only when the distance exceeded about 4·5 cm. did the repulsion usually

associated with a point discharge become manifest. The critical distance varied, I think, with the potential attained by the point.

(*c*) Professor Tyndall suggests as another reason for an unbalanced pressure that there is lack of symmetry whenever "the drag of the ion on the gas" is unequal to the force imposed upon it by the electric field; in particular he argues that, since an ion starting from rest near a pole does not acquire full speed immediately, its "suction" on the electrode it is leaving is proportionately reduced, and consequently a backward pressure may prevail. But surely, if we subscribe to the suction idea and terminology (which is questionable), we ought to take into account the fact that such ions will go on "sucking" longer than if they instantaneously acquired their viscous velocity; the total suction will be the same whether or not it takes an appreciable time to reach the steady state, because it depends only upon the total amount of momentum permanently communicated to the vapour molecules by the moving ions.

So it appears to me that there is here no valid cause of departure from a true balance. I am strengthened in this view by the fact that if we do assume that this type of dissymmetry can occasion a lack of balance and account for the observed pressure, we do not, as Tyndall himself has shown, obtain very probable values for the mobilities of the ions taking part in the phenomenon.

But it seems to me unnecessary to insist upon the dissymmetry hypothesis. Professor Tyndall and Mr. Beer explain certain of their observations upon the manometric pressure by the emission of positive and negative thermions from the hot poles, a feature which, in itself, would seem naturally to call for a recoil phenomenon.

Again, while I do not wish to imply that the projection theory is devoid of difficulties, it appears to me that Professor Tyndall's main objection to my theory arises from a misapprehension. Such evidence as I was able to obtain indicated that the particles responsible for the reaction were electrons, and I sought to fit this information into the scheme of the arc outlined in my paper upon "The Consumption of Carbon in the Electric Arc" (Roy. Soc. Proc. A. xcii. p. 122, 1915). From this investigation it seems definite that, near the cathode, electrons must carry either 0, $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$ or all the current. The pressure work limits us to one of the last four alternatives; all of these give values of e/m for the carrier of the order of magnitude associated with the electron rather than with the atom, but it happens that the value

obtained by assuming that $\frac{1}{2}$ the current near the cathode is borne by electrons gives the value agreeing best with the accepted value; and as this choice also seemed preferable for reasons stated in the above paper, it was this view to which I devoted most attention, though I did not, nor do I now, wish definitely to rule out the other alternatives, because the values obtained for e/m depend upon the distribution of the emitted electrons about the axis of the arc; and upon this point we require further information.

Now, all this argument deals with what takes place *at* or *in the immediate neighbourhood* of the cathode (as reference to pages 132 and 133 of Phil. Trans. Roy. Soc. A. 220. pp. 109–136, 1919, will confirm); but Professor Tyndall seems to have overlooked the force of the words I have here italicised, because his objection is based on his deduction that the number of positive and negative carriers *in the body of the arc* must be in the ratio of their mobilities, which would imply that if the negative carriers are electrons, they must carry 500 times as much current as the positives—practically the whole of the currrent. As he definitely excludes the region close to the poles from this category, there is no clear disagreement between our views. It seems to me certain that there will be intense ionization where the projected electrons meet the vapour molecules, especially as they suffer a further fall of some 11·6 volts just outside the cathode, possibly within their mean free path, and therefore that there should be liberated a sufficient number of electrons to carry the bulk of the current and to conform to the condition laid down by Professor Tyndall as pertaining to the body of the arc.

But I think it important to emphasize that the mechanism of the arc is determined chiefly by what goes on at the poles; it does not lead us far if we are content to treat it simply as a mass of gas between two electrodes. The clue to the mechanism of the carbon arc lies in the fact that for each carbon atom which is lost from the cathode of a very short arc, or a long one if extraneous losses are excluded, four electronic charges, or their equivalent, cross the arc-gap. Add to this the facts that the nature of the surrounding gas is of vital importance—we know, for example, that the arc depends for its existence upon interactions between the gas and the material of the poles,—that the maintenance of a hot cathode is essential, and that a certain minimum potential must be maintained across the terminals, depending to some extent upon the temperature we allow the anode to reach, and we have the necessary foundation upon which to erect our theory of the arc.

I do not think we can get away from the four main alternatives enumerated in the paper to which I have referred ; what we must do—what I have endeavoured to do—is to choose the view which fits the new information provided by the reaction observations. I venture to think that Professor Tyndall's contention has not rendered my explanation less probable ; there is nothing contrary to my theory in the manometric pressure-arc length curves upon which he has based his objection.

(2) *The evaporation of carbon atoms from the poles.*

Professor Sellerio, somewhat naively disclaiming any intention of dealing conscientiously with the problem, disregards all other alternatives, and considers that the observed pressure is the reaction consequent upon the evaporation of carbon atoms, a hypothesis which I had previously examined and rejected. Sellerio has, however, recalculated the reaction to be expected on new assumptions, and maintains that the result is substantially in agreement with observation. He dissents from my view that the carbon atoms upon evaporation issue with velocities of the order of magnitude of their atomic speeds appropriate to the temperature of the arc—that is to say, of boiling carbon. He gives reasons for preferring a velocity only 1/500 to 1/1000 of this, but his argument is based upon the erroneous supposition that the vapour is saturated upon emission. Some interesting spectrograms of a spark discharge were taken some years ago by Dr. Royds (Phil. Trans. Roy. Soc. 1908) upon a moving film ; each spectrum line was curved like a streamer, whose inclination was a measure of the velocity of the material as it crossed the gap. These velocities I find to be of the same order of magnitude as the atomic velocities calculated on the assumption that the poles are at the boiling-point of the material of which they are composed. Other evidence to the same effect will be found in a paper recently presented to the Editors of this Magazine.

Furthermore, as I hinted in a previous paper [4], no investigation of the evaporative reaction is complete which does not take into account the interaction of the projected material with the surrounding vapour. This I have recently attempted to do, and find that the reaction R may be simply calculated from the approximate expression $R=(Dv)^2/2\Pi A$ if the loss of weight D in gms. per second is small; here Π is the external pressure, A the area from which the discharge occurs, and v the velocity of projection. Applying this to the 10 amp. 6 mm. arc, we have for the cathode $A = 0{\cdot}096$ cm.^{2} (Sellerio); D is obtained from our previous

estimate of the carbon loss, $8{\cdot}5 \times 10^{-4}$ gm. per sec., of which, however, 66 per cent. occurs from the sides of the carbon and contributes nothing to the reaction; the remainder, $3{\cdot}1 \times 10^{-4}$ gm., is the value of D. This gives R (cathode) = ·04 dyne. Similarly for the anode, even if we suppose half the total loss to take place from the crater, which is an overestimate, we find R (anode) = ·07 dyne. These values are far too small to account for the observed pressure, namely 2·18 and 2·10 dynes respectively.

Even if we were to suppose that the whole loss of carbon assists in producing the reaction, and that it all takes place from the small areas upon the poles from which the arc springs, the corresponding forces would be ·33 and ·29 dyne respectively, still smaller than the observed values; we have, moreover, the contrary evidence that the forces upon the poles remain constant or diminish to a minimum value as the arc length increases, whereas the total loss of carbon increases to a maximum for both poles.

We calculated [3] our value of e/m on the assumption that the projected material did not interfere appreciably with the momentum delivered to the poles by the vapour of the arc—whose undisturbed arrival should provide the ordinary atmospheric pressure upon it,—and found that e/m was of the order of magnitude associated with the electron. This means that the electrons do not to any large extent impart momentum to the vapour molecules as they pass through the arc; when they ionize the vapour, their momentum is in the main handed on to the electrons to which they give rise. A small loss of momentum would not, however, appreciably affect the calculated order of magnitude of e/m.

On the other hand, if we suppose that the projected material does interfere with the external atoms, we must substitute for our equation (1) (Phil. Trans. Roy. Soc. A. 220. p. 131, 1919) the expression

$$\sqrt{3}p = (mnv)^2/2\Pi A,$$

which gives us

$$e/m = VC^2/\sqrt{3}\Pi A p,$$

which for the cathode leads to $e/m = 1690$, which is reasonably close to the value of e/m for a carbon atom carrying two electronic charges, namely 1600.

The corresponding value for the velocity v is $1{\cdot}43 \times 10^6$ cm./sec., which is some 5 times greater than the atomic velocity, $2{\cdot}97 \times 10^5$ cm./sec., for carbon vapour at 4000° C. I do not wish to state definitely that this is an impossible

value, since a few of the lines for metals measured by Royds (*loc. cit.*) gave values for v about 5 times as great as the velocity of atomic agitation at the boiling-point, but in these cases there were always other and stronger lines which provided values nearly equal to the temperature velocities. Still, the matter is in an interesting stage; it would open up new difficulties if the vapour in the arc were to receive so much of the momentum of the projected material that only a few per cent. reached the opposite pole, or were effective in producing a recoil upon the pole from which the material was originally derived.

I therefore submit that in the present state of our knowledge the evidence is against the evaporation of carbon being the main cause of the phenomenon, though I do not think it quite negligible. Indeed, in the particular state of the iron arc which I characterized as turbulent, as distinct from the normal quiescent arc, I believe it plays the predominant part. Even in the case of the carbon arc, more exact information regarding the sizes of the hot spots might cause us to revise our conclusions. We can, however, only deal with the evidence before us.

(3) *On the relationship between the manometric and mechanical pressures.*

One hesitates to criticize the deductions made by an observer from his own experiments, but I think it important to suggest, though I scarcely expect Prof. Tyndall to agree with me, that it does appear from his and Mr. Beer's important experiments[7] upon the manometric pressure within the arc that this arises from the same cause as that which produces the mechanical reaction upon the poles, namely the projection of particles from the cathode.

If we accept electronic projection from the cathode, what manometric pressures should we expect at the two poles? At the cathode, if the hole is central and small enough to be completely within the hot spot, there will be high-speed electrons projected from the walls of the tube more or less normally, and these will occasion a positive pressure there; if the hole is not central or too large to be completely covered, we should expect the electrons projected from the end to impart some at least of their momentum to the gas molecules, which will thus be withdrawn from the tube leading to the manometer, causing it to record a reduced pressure. At the anode the arrival of negative ions should occasion an increase of pressure, and, as the hot spot is large, this would be

observed with much larger holes than could be used in the cathode.

This is precisely what Tyndall and Beer observed. They also found that, when definite results were obtainable, the manometric pressure increased with the current just as the mechanical pressure does, and that the variation of hydrostatic pressure at the anode agreed with our Series B curves. In addition they occasionally noted a very minute negative pressure at the anode when the current was very small and the hole large and non-central; this I should ascribe either to convection currents, which were certainly not negligible in my experiments, or, as Tyndall and Beer regard it, to the effect of thermionic projection there.

Nor is the magnitude of the manometric effect out of keeping with the view that it is due to an electronic discharge from the cathode*. Taking, for obvious reasons, the *maximum* positive pressure observed in a hole in the cathode, namely 24·7 dynes per sq. cm. for a current of 13·5 amps., which is equivalent to $24{\cdot}7 \times 10/13{\cdot}5$ dyne/cm.^{2} for a 10 amp. arc, we see that, since the area of the hot spot is 0·096 cm.^{2}, according to Sellerio, the reaction upon the whole arc should be $24{\cdot}7 \times 0{\cdot}096 \times 10/13{\cdot}5$ or 1·76 dyne, which is in reasonable agreement with the 2·1 dynes which we observed; it is certainly of the right order of magnitude.

The manometric pressure at the anode observed by Tyndall and Beer was 8·8 dyne/cm.^{2} for a current of 10 amperes (measured from their curve "D"). The area of the crater being 0·31 cm.^{2} (Sellerio), the reaction to be expected is $8{\cdot}8 \times 0{\cdot}31 = 2{\cdot}73$ dynes; this is somewhat in excess of the mechanical pressure observed by Burnham, Davis, and myself, but remarkably close considering the difficulties of estimating the size of hole and of crater, and considering also that the presence of the hole must somewhat modify the conditions within the arc.

We note further that the "suction" at the cathode was observed by Tyndall and Beer to be much less numerically than the positive manometric pressure at the anode, the ratio for a 10-ampere arc being rather less than 1 to 4. This is in keeping with our view that the bulk of the momentum is conveyed across the arc to the anode without imparting it to the vapour molecules.

Dundrennan, Glenelg,
South Australia,
Feb. 1923.

* The approximate quantitative agreement was first pointed out by Sellerio [9] though he did not suggest that the effects were otherwise related.—D. G.

CXX. *A Theory of the Abnormal Cathode Fall.* *By* The Research Staff of the General Electric Co., Ltd., London *. (*Work conducted by* J. W. Ryde.)

Summary.

A THEORY of the abnormal cathode fall is given, according to which conduction in the dark space is closely analogous to that in a high vacuum between a plane thermionic cathode and plane anode. According to the theory, the width of the dark space with given current and voltage should be determined by the atomic weight of the gas and universal constants.

The theory is compared with the measurements of Aston and of Aston and Watson. The relatively small divergence between the simple theory and experiment can be removed, partially at least, by taking into account the electrons liberated at the cathode, information concerning which is given by Cheney's measurements, and the collisions of the positive ions with neutral molecules.

But it seems difficult to reconcile the theory with Aston's determination of the variation of the electric field through the dark space.

ALL theories of the cathode fall with which we are acquainted assume that it is determined largely by collisions of the positive ions with neutral molecules within the cathode dark space. The assumption is made either when it is assumed that the velocity of the ions at any point is proportional to the field there, or when it is assumed that the cathode fall is determined by the ionization potential.

So far as the normal cathode fall is concerned (and it is to the normal fall that such theories have usually been directed) the assumption is probably correct. But in a recent paper we have shown that there is some reason for believing that it is not correct in the abnormal fall. The cathodic disintegration, which increases so very greatly in the passage from the normal to the abnormal fall, seems explicable only if, when the fall is abnormal, the positive ions arrive at the cathode with nearly the full velocity corresponding to the fall; their velocity has not been greatly reduced by collisions. Accordingly, it seems worth while to proceed to the other extreme and to discuss the abnormal cathode fall on the assumption that there are no collisions. Doubtless the assumption is not exactly true, but it may be

* Communicated by the Director.

possible to introduce the effect of the collisions as a small correction to a theory based on ignoring them.

It is known that the intensity of the field is very small at the boundary between the dark space and the cathode glow. Let us assume that the division between the dark space and the glow is a definite plane, parallel to the plane cathode, and that in this plane the field is zero. Physically, the assumption is possible, for it implies that the number of positives disappearing by recombination in the glow is very large compared with the number dragged out of it to the cathode by the field; and the luminosity of the glow indicates that recombination is proceeding rapidly. Now, if these assumptions are made, the problem of determining the relation between the current through the dark space, the potential difference across it, and the distance between its boundaries is precisely analogous to that of determining the corresponding relation for a plane thermionic cathode in a high vacuum. To the electrons in the thermionic case correspond the positive ions, to the hot cathode at which $dV/dx=0$ corresponds the boundary between the negative glow and dark space, and to the cathode corresponds the anode. It is well known that the relation is given by

$$di^{1/2}=kV_1^{3/4}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$k^4=\frac{2}{81\pi^2}\frac{e}{m_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here i is the current, d the distance, and V_1 the potential difference between the electrodes, e and m_1, the charge and mass of the carriers, which are now the positive ions of the gas in the discharge-tube, and not electrons.

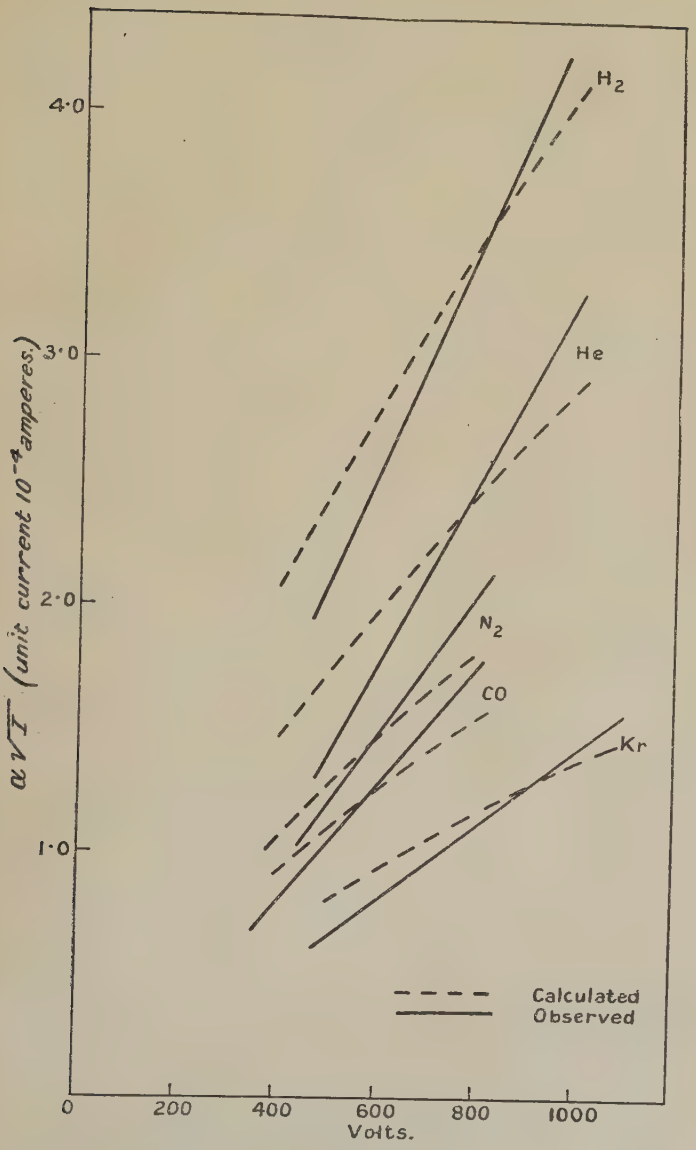
The relation between V_1, i, d has been determined experimentally for a number of gases by Aston and Aston and Watson *, who expressed their results by the empirical formula

$$di^{1/2}=k_1(V-G), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which differs in form from (1) only by the substitution of $V-G$ for $V^{3/4}$, where G and k_1 are constants, determined by the gas and the material of the cathode. We have calculated the relation between $di^{1/2}$ and V_1, first from the empirical equation (3), which represents directly the experimental results with aluminium electrodes (see p. 1155), and second from our equation (1), which contains, beyond the

* F. W. Aston, Proc. Roy. Soc. A. lxxix. p. 80 (1907); F. W. Aston and H. E. Watson, *ib.* A. lxxxvi. p. 168 (1912).

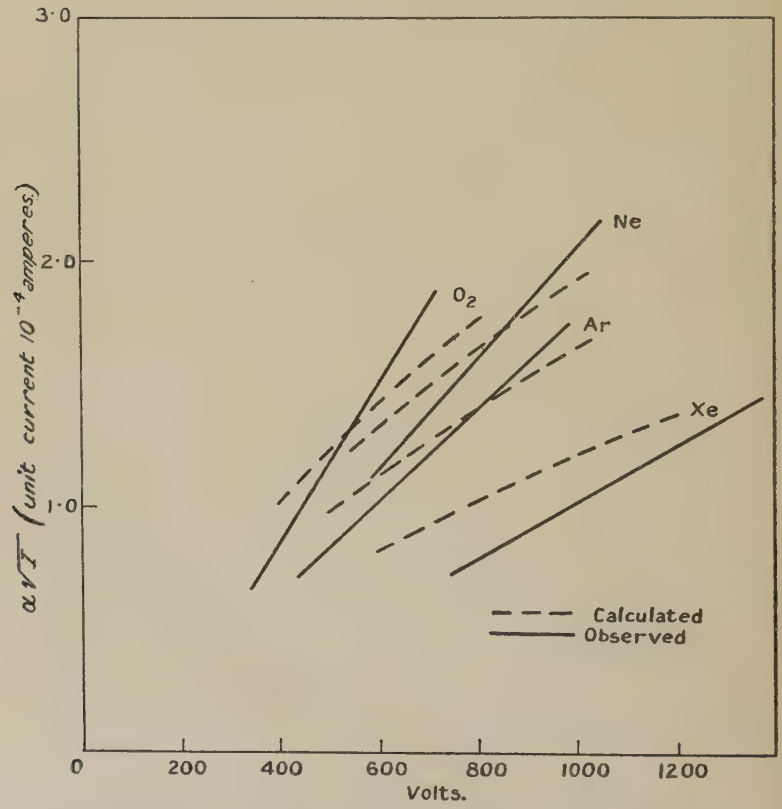
Fig. 1.



atomic weight of gas, nothing but universal constants. The results are indicated in figures 1, 2, where the full lines give the observed results; the dotted lines the calculated results.

It is obvious at once that observation and calculation do not wholly agree; and we do not pretend that they do or suggest that they ought to agree. But we would point out that they agree in order of magnitude, and that the relation between the observed and calculated lines is of the same nature for all the gases. They all cross at about the

Fig. 2.



same angle and in the same region of voltage. We draw the conclusion that in general outline our theory is correct, and that the remaining discrepancy is due to some factors of minor importance that we have neglected.

There are two such factors. First, there are the electrons liberated by the positives when they impinge on the cathode; second, there are collisions of the positive ions, and perhaps of the electrons, with the neutral molecules. We will discuss them in turn.

The electrons from the cathode will have two effects on the relation in question. They will carry some of the current, and, by neutralizing partially the space charge, they will permit more positives to cross under the same field. It is easily shown that the second effect is wholly negligible. For, with the notation usual in the analogous case and putting $V=x=0$ at the boundary between dark space and glow, we have

$$\frac{d^2V}{dx^2} = -4\pi e(n_+ - n_-), \quad . \quad . \quad . \quad . \quad (4)$$

$$i = e(n_+v_1 + n_-v_2), \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\tfrac{1}{2}m_1v_1^2 = eV, \qquad \tfrac{1}{2}m_2v^2 = e(V_1 - V). \quad . \quad . \quad (6)$$

If each positive ion causes the emission of q electrons from the cathode,

$$n_-v_2 = qn_+c_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Proceeding in the usual manner we find

$$\left(\frac{dV}{dx}\right)^2 = \frac{ai}{q+1}\{V^{1/2} + b(V_0 - V)^{1/2} - bV_0^{1/2}\}, \quad . \quad (8)$$

where

$$a = 8\sqrt{2}\pi\left(\frac{m_1}{e}\right)^{1/2}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$b = q\left(\frac{m_2}{m_1}\right)^{1/2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Now, q is not greater than 0·1, $\frac{m_2}{m_1}$ not greater than ·0006; hence b is not greater than ·002. But b is the maximum ratio of the sum of the last two terms in the bracket to the first. It is clear then that b may be neglected and that the only appreciable effect of the electrons from the cathode is represented by the q outside the bracket. In other words, though these electrons carry an appreciable fraction of the current, they do not alter the field appreciably.

Accordingly, the only change in (1) necessary is the substitution of $i/(q+1)$ for i, so that now

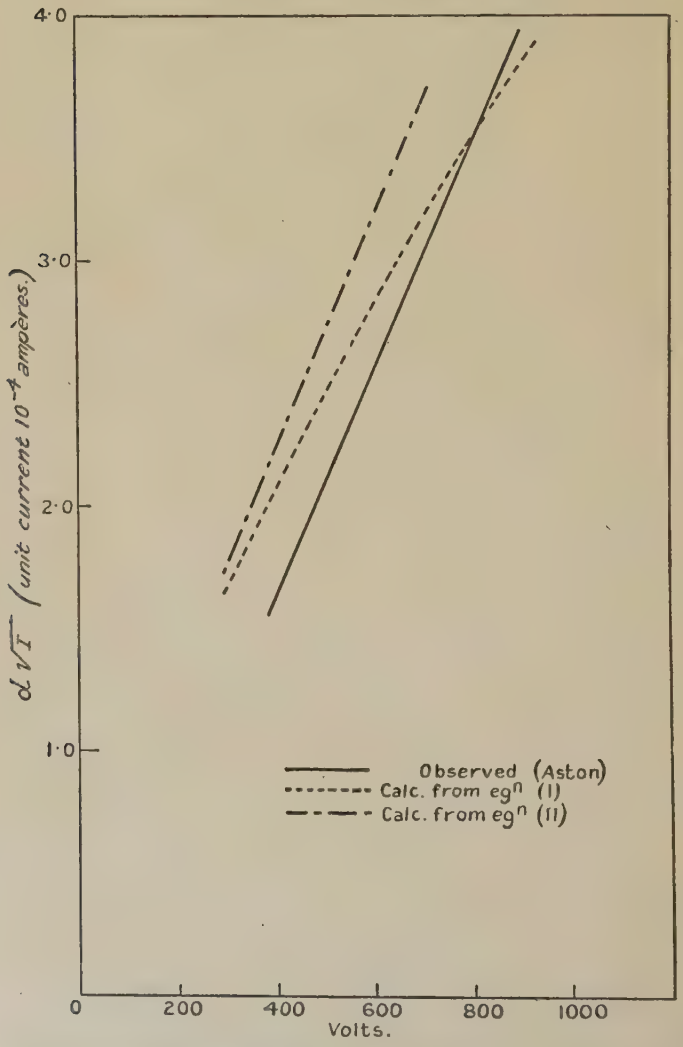
$$di^{1/2} = k(q+1)^{1/2}V_1^{3/4}. \quad . \quad . \quad . \quad . \quad (11)$$

q can be estimated from the observations of Cheney *. It is determined by the speed and nature of the ions and of the material of the cathode. Unfortunately, Cheney's results refer only to lithium, potassium, and rubidium ions; but it appears from them that q for hydrogen should not be very

* W. L. Cheney, Phys. Rev. x. p. 335 (1917).

different from that for lithium. Using Cheney's value of q for lithium and an aluminium cathode, we may recalculate from (11) the relation for hydrogen and the same cathode,

Fig. 3.—Hydrogen with Aluminium Cathode.



and compare it with Aston's measurement. In fig. 3 the full line is that observed, the dotted curves those calculated from (1) and (11).

It will be seen that the introduction of q makes the

observed and calculated lines almost parallel, but the latter is definitely higher. It is unfortunate that Aston's* measurements on cathodes other than aluminium were made without guard-rings, and are therefore not comparable with the theoretical equations, and that q is not known for other positive ions. But qualitatively the influence of the material of the cathode and of the nature of the ions is always in the direction indicated by (11) and by Cheney's values of q.

It remains to be explained why the values of $di^{1/2}$ given by (11) are uniformly greater than those observed. The discrepancy is doubtless partly due to the fact that Aston's V is the difference of potential between anode and cathode, while ours is that between negative glow and cathode, and is therefore slightly smaller. But the presence of the neutral molecules must be taken into account. The electrons produced by ionization will not be important, for they are few in number compared with those from the cathode. However, the loss of energy of the positive ions at collisions may be appreciable. It will produce an effective decrease of V or increase of m_1, and will therefore bring the calculated line nearer to the experimental. But we have not succeeded in making an estimate of their effect sufficiently accurate to enable a numerical comparison to be made. We hope, however, in the future to throw further light on the matter by determining by means of sputtering with what velocity the positive ions actually strike the cathode.

One further discrepancy remains. Aston found that in the dark space $d\mathrm{V}/dx$ was proportional to x; according to (8) it should be proportional to $x^{1/3}$. No explanation can be offered at present; reduction of the energy of the positive ions by collisions with neutral molecules must change somewhat the distribution of the field, but it seems difficult to believe that it could distort it so completely as Aston's measurements indicate without at the same time changing the currents so as to remove all agreement between experiment and theory. However, whatever may be the solution of this difficulty, we feel that sufficient evidence has been produced that with abnormal cathode fall, the width of the dark space is determined mainly by the atomic weight of the gas, and that the positive ions arrive at the cathode with very nearly the velocity corresponding to the full cathode fall.

We take this opportunity of correcting an error in a previous paper, Phil. Mag. xlv. pp. 99–112, 1923. On p. 102, l. 3, *for* "$m'/\mathrm{C}' = \text{constant}$", *read* "$m'\mathrm{C}' = \text{constant}$".

* F. W. Aston, Proc. Roy. Soc. A. lxxxvii. p. 437 (1912).

CXXI. *Extended Application of the Principle of Stationary Phase in Wave-Motion Problems.* *By* GEORGE GREEN, *D.Sc.**

IN a former paper under the title "On Group-Velocity and on the Propagation of Waves in a Dispersive Medium" †, the theory of group-velocity is discussed from the standpoint of the late Lord Kelvin's paper of 1887, "On the Waves produced by a Single Impulse in Water of any Depth, or in a Dispersive Medium." The theory of group-velocity contained in this paper is essentially the same as the principle of "stationary phase" frequently employed in optical and other waves problems. This principle is illustrated in the above paper in the evaluation of the integral

$$\xi=\frac{1}{2\pi}\int_0^\infty dk\cos\left[k\{x-\mathrm{V}t\}\right]:\quad \mathrm{V}=f(k),\quad .\quad .\quad (1)$$

expressing the effect at any point x at time t of an impulse delivered at the origin at time zero in any dispersive medium. For each Fourier train represented in the above integral by a definite value of k, we have the wave-length $\lambda=\frac{2\pi}{k}$, the wave-velocity $\mathrm{V}=f(k)$, and the phase $\phi=[k(x-\mathrm{V}t)]$ at point x at time t. The condition that the phase of the constituent Fourier trains is stationary in the neighbourhood of a definite value k_0 at point x at time t is

$$\frac{d\phi}{dk}=x-\frac{d(k\mathrm{V})}{dk}t=0,\quad \text{or}\quad x=\{f(k_0)+k_0f'(k_0)\}t.\quad .\quad (2)$$

Thus the point of the medium at which the wave-length $\frac{2\pi}{k_0}$ predominates changes its position with velocity, $\mathrm{U}=\{f(k_0)+k_0f'(k_0)\}$, where U is the group-velocity corresponding to wave-length $\frac{2\pi}{k_0}$.

According to the principle of "stationary phase," the wave-trains which contribute effectively to the resultant displacement of the medium ξ, at point x at time t, are those included in a narrow range of k on either side of k_0: and the phase ϕ within this range may be represented accurately by

* Communicated by the Author.
† Proc. R. S. E. vol. xxx. (1909).

a few terms of the series

$$\phi = [k\{x - Vt\}] = k_0\{x - f(k_0)t\} + (k - k_0)\frac{d\phi}{dk_0} + \frac{(k-k_0)^2}{2!}\frac{d^2\phi}{dk_0^2} + \frac{(k-k_0)^3}{3!}\frac{d^3\phi}{dk_0^3} + \text{etc.}$$

$$= a_0 + \frac{b_0}{2!}\sigma^2 + \frac{c_0}{3!}\sigma^3 + \text{etc.}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which $\frac{d\phi}{dk_0} = 0$, and we have put σ instead of $k - k_0$.

Outside the effective range the phase varies rapidly with k, and the quantity to be integrated consists of a large number of positive and negative parts whose total effect is very small. Within the effective range of k on either side of k_0, the number of terms of the series required to represent the phase ϕ with sufficient accuracy depends upon the relative values of the successive terms. The case treated by Lord Kelvin in the paper above referred to, and by later writers also, is that in which $\frac{d^2\phi}{dk^2}$ is large compared with any term coming after it. The evaluation given by Lord Kelvin is therefore restricted in its application to certain definite ranges of x and t within which the term $\frac{d^3\phi}{dk^3}$ is exceedingly small compared with $\frac{d^2\phi}{dk^2}$. The evaluation given by Lord Kelvin is contained in the statements

$$\xi = \frac{1}{2\pi}\int_0^\infty dk \cos\phi = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\sigma \cos\left[a_0 + \frac{b_0}{2!}\sigma^2\right]$$

$$= \frac{1}{(\pm 2\pi b_0)^{\frac{1}{2}}}\cos\left(a_0 \pm \frac{\pi}{4}\right), \quad . \quad . \quad (4)$$

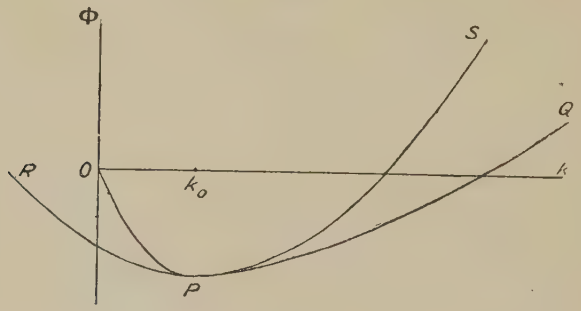
the negative sign being taken when b_0 is negative.

The process here employed virtually consists in replacing the curve OPQ in fig. 1, representing the true phase over the whole range of k from zero to infinity, by a curve, RPS, which coincides with the true phase-curve only in the immediate neighbourhood of k_0, the point at which the phase is stationary for variations in k. On account of the rapid variation in phase on the assumed phase-curve beyond a very small range on either side of k_0, the contribution to the total value of the integral depending on these parts of the curve is very small, just as in the case of the true phase-curve. The same reasoning justifies the infinite limits in the case of

the auxiliary curve, provided k_0 is not itself a very small quantity. When k_0 is a small quantity, the lower limit of the integral is not $-\infty$ but $-k_0$ if a slightly better approximation than that given in (4) is required.

The evaluation given above applies to the case where, at point x at time t, the phase-curve has one point of stationary phase. The range of values of x and t to which the result applies depends on the closeness of the agreement between the auxiliary phase-curve and the true phase-curve over a considerable range of values of k. This agreement between the two curves near the stationary point is, of course, improved

Fig. 1.

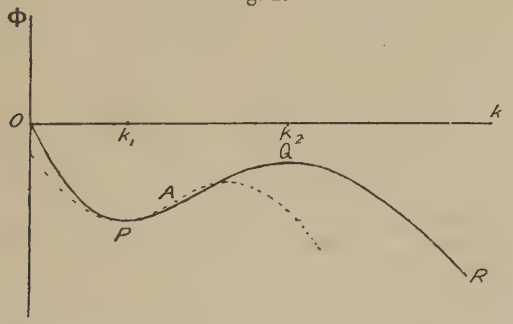


by the inclusion of the term $\frac{d^3\phi}{dk_0^3}$ in the series, but the new auxiliary curve is now of a different type from the original curve, being a curve with a point of inflexion and two stationary points, and it is accordingly unsuitable for use over the full range of integration.

When however the phase-curve itself has two points, k_1 *and* k_2, at which the phase is stationary as in the curve OPQR of fig. 2, the third term in the series must be included in order to obtain the necessary agreement between the auxiliary phase-curves and the true phase-curve. In this case the $\frac{d^3\phi}{dk^3}$ term is not small compared with the $\frac{d^2\phi}{dk^2}$ term, and may become the predominant term. This occurs when the two roots of $\left(\frac{d\phi}{dk}=0\right)$ become very close, or pass into coincidence when therefore $\frac{d^2\phi}{dk^2}$ becomes zero altogether. The intention of the present paper is to discuss fully the

evaluation of ξ when the $\frac{d^3\phi}{dk^3}$ term is included in the expression for the auxiliary phase-curve. The discussion applies to all cases where there are maxima or minima of the group-velocity, and contains the extension referred to by Lord Kelvin at the close of his paper, where he remarks "The working out of our present problem for this case, or any case in which there are either minimums or maximums, or both maximums and minimums, of wave-velocity, is particularly interesting, but time does not permit of its being included in the present communication."

Fig. 2.



Let us take the curve represented in fig. 2 to be the true phase-curve, k_1 and k_2 being the two stationary points at which $\frac{d\phi}{dk}=0$. The auxiliary phase-curve exactly agreeing with this curve in the neighbourhood of k_1 is given by

$$\phi_1=a_1+\frac{b_1}{2!}\sigma^2-\frac{c_1}{3!}\sigma^3, \quad . \quad . \quad . \quad . \quad (5)$$

and that agreeing with the true curve in the neighbourhood of k_2 is given by

$$\phi_2=a_2-\frac{b_2}{2!}\sigma^2-\frac{c_2}{3!}\sigma^3. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The dotted curve shown in the figure represents the auxiliary curve at k_1. When k_1 and k_2 are nearly equal, it follows from Taylor's expansion that all three curves agree over the full range between k_1 and k_2, but in general, with k_2-k_1 large, the agreement of each curve with the true phase-curve ceases to be sufficiently good beyond the point of inflexion. On the auxiliary curve at k_1, the point of inflexion occurs when $(k-k_1)$ has the value $+\frac{b_1}{c_1}$ and the

curve itself is symmetrical about its point of inflexion. Similarly, on the auxiliary curve at k_2 the point of inflexion occurs when $k-k_2$ has the value $-\frac{b_2}{c_2}$, and this curve also is symmetrical about its own point of inflexion. If now we employ the auxiliary phase-curve for k_1 for integration up to its point of inflexion and the auxiliary phase-curve for k_2 for integration from its point of inflexion outwards to infinity, we shall obtain a value for the complete integral similar to that obtained by Lord Kelvin for the case of a single point of stationary phase on the true phase-curve. When $\frac{b_1}{c_1}$ is exceedingly large, the point of inflexion A on the first auxiliary curve at k_1 is far removed from k_1, and the whole integration in which the k_1 curve is employed corresponds exactly to the case dealt with by Lord Kelvin except in this, that the auxiliary phase-curve used contains the additional terms depending upon c_1. In this case also the same remark applies to the integration in which the k_2 auxiliary phase-curve is employed.

According to the above an approximate value for the integral appearing in (1) may be obtained by writing

$$\xi=\frac{1}{2\pi}\int_{-k_1}^{+\frac{b_1}{c_1}}\cos\phi_1 d\sigma+\frac{1}{2\pi}\int_{-\frac{b_2}{c_2}}^{\infty}\cos\phi_2 d\sigma=\xi_1+\xi_2, \quad . \quad (7)$$

where ϕ_1 and ϕ_2 are given by (5) and (6) respectively. By means of the substitution

$$\frac{\pi}{2}w^3=\frac{c_1}{3!}\left(\sigma-\frac{b_1}{c_1}\right)^3$$

in the first of the above integrals, and of the substitution

$$\frac{\pi}{2}w^3=\frac{c_2}{3!}\left(\sigma+\frac{b_2}{c_2}\right)^3$$

in the second, each of the auxiliary phase-curves is referred to an origin at its point of inflexion, and (7) is transformed into

$$\xi=\frac{1}{2\pi}\left\{\frac{\pi}{2}\frac{3!}{c_1}\right\}^{1/3}\int_{-\alpha}^{0}dw\cos\left[\left(a_1+\frac{1}{3}\cdot\frac{b_1^3}{c_1^2}\right)-\frac{\pi}{2}(w^3-m_1w)\right]$$
$$+\frac{1}{2\pi}\left\{\frac{\pi}{2}\cdot\frac{3!}{c_2}\right\}^{1/3}\int_{0}^{\infty}dw\cos\left[\left(a_2-\frac{1}{3}\frac{b_2^3}{c_2^2}\right)-\frac{\pi}{2}(w^3-m_2w)\right], \quad . \quad . \quad . \quad (8)$$

where

$$\alpha = \left\{\frac{2}{\pi}\cdot\frac{c_1}{3!}\right\}^{1/3}\left(k_1+\frac{b_1}{c_1}\right).$$

$$m_1 = \frac{1}{3}\left(\frac{2}{\pi}\right)^{2/3}\left(\frac{3!}{c_1}\right)^{4/3}\left(\frac{b_1}{2!}\right)^2, \quad m_2 = \frac{1}{3}\left(\frac{2}{\pi}\right)^{2/3}\left(\frac{3!}{c_2}\right)^{4/3}\left(\frac{b_2}{2!}\right)^2.$$

When the points of stationary phase coincide at k_1, we have $a_1=a_2$, $b_1=b_2=0$, $c_1=c_2$, $m_1=m_2=0$, and

$$\xi = \frac{1}{2\pi}\left\{\frac{\pi}{2}\frac{3!}{c_1}\right\}^{1/3}\int_{-\alpha}^{\infty} dw \cos\left[a_1-\frac{\pi}{2}w^3\right]. \quad . \quad . \quad . \quad (9)$$

When α is assumed to be very large, as in the cases treated by Lord Kelvin, we may put $\alpha=\infty$, and then we have for the special case considered in (9),

$$\xi = \frac{1}{2\pi}\left\{\frac{\pi}{2}\cdot\frac{3!}{c_1}\right\}^{1/3}\cos a_1\int_{-\infty}^{+\infty} dw\cos\frac{\pi}{2}w^3, \quad . \quad . \quad . \quad (10)$$

which is the same as a result given by the late Lord Rayleigh* and by T. H. Havelock †.

For the complete evaluation of ξ in (8) we require the values of the integrals

$$\int_0^{\alpha} dw\cos\frac{\pi}{2}(w^3-mw) \quad \text{and} \quad \int_0^{\alpha} dw\sin\frac{\pi}{2}(w^3-mw)$$

for values of α finite and infinite ‡. Each of these integrals is a function of m, $\mathrm{I}(m)$, such that $\mathrm{I}(0)$ and its derivative $\mathrm{I}'(0)$ may be regarded as known, being defined by well-known integrals. Each integral also, regarded as a function of m, satisfies a differential equation of the form

$$\frac{d^2\mathrm{I}}{dm^2}+\left(\frac{\pi}{2}\right)^2\cdot\frac{m}{3}\mathrm{I}=\mathrm{C}\ (\text{a constant}): \quad . \quad . \quad . \quad (11)$$

and the values of the above integrals are readily obtained by first writing down the complete solution of this equation and then determining the two arbitrary constants by means of the known values of $\mathrm{I}(0)$ and $\mathrm{I}'(0)$. In the present paper we shall put down the results only for the case of $\alpha=\infty$, as the corresponding results for α finite can be readily written

* Scientific Papers, vol. vi. p. 10.

† Phil. Trans. lxxxi. (1908).

‡ The cosine integral has been evaluated in the form of a series by Stokes, who has also established the convergency of the integrals (Mathematical Papers, vol. ii. p. 329). The cosine integral has also been evaluated by Wirtinger, in 'Zwei Bemerkungen zu Airy's Theorie des Regensbogens,' by the method employed in the present paper.

down by the method employed here when we come to discuss particular problems in which these integrals are required. The complete solution of equation (11) is given by

$$I(m)=Am^{1/2}J_{-1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}+Bm^{1/2}J_{1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}+CF(m), \quad . \ . \ . \ (12)$$

where

$$F(m)=\frac{m^2}{1.2}-\frac{pm^5}{1.2.4.5}+\frac{p^2m^8}{1.2.4.5.7.8}-\text{ etc.}:$$

$$\text{and } p=\left(\frac{\pi}{2}\right)^2\cdot\frac{1}{3}. \quad . \ . \ . \ (13)$$

For the integral $\int_0^\infty dw\cos\frac{\pi}{2}(w^3-mw)$;

$$C=0, \quad I(0)=\frac{1}{2\sqrt{3}}\left(\frac{2}{\pi}\right)^{1/3}\Gamma\left(\frac{1}{3}\right), \quad I'(0)=\frac{1}{2\sqrt{3}}\left(\frac{\pi}{2}\right)^{1/3}\Gamma\left(\frac{2}{3}\right).$$

For the integral $\int_0^\infty dw\sin\frac{\pi}{2}(w^3-mw)$;

$$C=-\frac{\pi}{6}, \quad I(0)=\frac{1}{6}\left(\frac{2}{\pi}\right)^{1/3}\Gamma\left(\frac{1}{3}\right), \quad I'(0)=-\frac{1}{6}\left(\frac{\pi}{2}\right)^{1/3}\Gamma\left(\frac{2}{3}\right).$$

The values of these integrals are accordingly given by

$$\int_0^\infty dw\cos\frac{\pi}{2}(w^3-mw)$$

$$=\frac{\pi}{3}\cdot\left(\frac{m}{3}\right)^{1/2}\left[J_{-1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}+J_{1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}\right], \ . \ (14)$$

and

$$\int_0^\infty dw\sin\frac{\pi}{2}(w^3-mw)$$

$$=\frac{\pi}{9}\cdot m^{1/2}\left[J_{-1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}-J_{1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right]\right\}-\frac{\pi}{6}F(m).$$

$$. \ . \ . \ (15)$$

The expressions which we have obtained for the sine and cosine integrals are useful for calculation when the quantity m is small in value. When m is large we can employ the asymptotic expressions for the Bessel's functions, but an asymptotic value for the function $F(m)$ is also required,

and it can be obtained by means of the integral

$$\int_0^\infty dw\, e^{-\frac{\pi}{2}(w^3+mw)}.$$

If we first expand $e^{-\frac{\pi}{2}mw}$ and integrate term by term; and if we expand $e^{-\frac{\pi}{2}w^3}$ and then integrate term by term; we obtain two different expressions for the value of the integral:

$$\int_0^\infty dw\, e^{-\frac{\pi}{2}(w^3+mw)}$$

$$= \frac{2\pi}{9} m^{1/2}\left[J_{-1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\} - J_{1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}\right] + \frac{\pi}{6} F(m)$$

$$= \frac{\pi}{6}\left(\frac{1}{pm} - \frac{1.2}{p^2m^4} + \frac{1.2.4.5}{p^3m^7} - \text{etc.}\right). \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Eliminate $F(m)$ from (15) by means of this equality, and we have the asymptotic value for the sine integral given by

$$\int_0^\infty dw \sin\frac{\pi}{2}(w^3-mw)$$

$$= \frac{\pi}{3} m^{1/2}\left[J_{-1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\} - J_{1/3}\left\{\pi\left(\frac{m}{3}\right)^{3/2}\right\}\right]$$

$$- \frac{\pi}{6p}\left(\frac{1}{m} - \frac{1.2}{pm^4} + \text{etc.}\right). \quad . \quad . \quad (17)$$

Taking only the first term of the well-known asymptotic values for the Bessel functions, we find, for m exceedingly large,

$$\int_0^\infty dw \cos\frac{\pi}{2}(w^3-mw) = \frac{2^{1/2}}{(3m)^{1/4}} \cos\left\{\pi\left(\frac{m}{3}\right)^{3/2} - \frac{\pi}{4}\right\}:$$

$$\int_0^\infty dw \sin\frac{\pi}{2}(w^3-mw) = -\frac{2^{1/2}}{(3m)^{1/4}} \sin\left\{\pi\left(\frac{m}{3}\right)^{3/2} - \frac{\pi}{4}\right\}, \quad (18)$$

in agreement with a result given by Stokes *.

The above results enable us to evaluate the integrals contained in (8) for the case where $\alpha=\infty$; that is, where k_1 is large, and so to determine ξ. It is interesting to note that

* *Ibid.* p. 341, equation (23).

when m_1 and m_2 become very large the portions of the auxiliary phase-curves employed in the integrations extend to infinity on both sides of the point at which the phase is stationary. Taking for example the second integral in (8), with m_2 very large, we can readily verify that its value is given by

$$\xi_2 = \frac{1}{2\pi}\left\{\frac{\pi}{2}\cdot\frac{3!}{c_2}\right\}^{1/3}\cdot\cos\left[\left(a_2 - \frac{1}{3}\frac{b_2{}^3}{c_2{}^2}\right) + \left\{\pi\left(\frac{m}{3}\right)^{3/2} - \frac{\pi}{4}\right\}\right]\cdot\frac{2^{1/2}}{(3m)^{1/4}}, \quad . \quad (19)$$

or, since

$$\pi\left(\frac{m}{3}\right)^{3/2} = \frac{1}{3}\frac{b_2{}^3}{c_2{}^2},$$

by

$$\xi_2 = \frac{1}{(2\pi b_2)^{1/2}}\cos\left[a_2 - \frac{\pi}{4}\right], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

which coincides with the result given by (4) for a phase-curve having one point at which the phase is stationary. When the two stationary points k_1, k_2 are widely separated, we have proved that the result given by (8) is equivalent to the result obtained by applying Lord Kelvin's evaluation given in (4) at each point of stationary phase separately, as already pointed out. By means of (14) and (15), and the corresponding results obtained for α finite, we can accordingly evaluate ξ for all curves of the type shown in fig. 2, whether the points of stationary phase are very near each other or the reverse.

In the general case an auxiliary phase-curve of the type

$$\phi = a + \frac{b}{2!}\sigma^2 + \frac{c}{3!}\sigma^3$$

can only be used to represent a curve with one point of stationary phase over a limited range. Beyond the point of inflexion on the auxiliary curve its form differs entirely from that of the curve it is intended to replace. Similarly, if we take four terms of equation (3),

$$\phi = a + \frac{b}{2!}\sigma^2 + \frac{c}{3!}\sigma^3 + \frac{d}{4!}\sigma^4,$$

to represent a phase-curve having only one point of stationary

phase, the auxiliary phase-curve can only represent the original curve between two points of inflexion on the auxiliary curve. Provided the portion of the auxiliary curve employed is of the same type as the original phase-curve, the results obtained by means of the auxiliary curve are more and more exact as the terms containing higher and higher powers of σ are included in the auxiliary phase-curve. This is well illustrated in the application of the stationary phase principle to derive the asymptotic expressions for the Bessel functions. The first term of this expression has already been derived by the late Lord Rayleigh * by means of the result given in (4). Taking the function,

$$J_n(z)=\frac{1}{\pi}\int_0^{\pi} d\omega \cos\{z\sin\omega-n\omega\}, \quad . \quad . \quad . \quad (21)$$

we require an expression for its value when z is very large, and n is small compared with z. The phase $\{z\sin\omega-n\omega\}$ is stationary at the value of ω given by $\cos\omega_1=n/z$, and the auxiliary phase-curve is represented by

$$(z\sin\omega-n\omega)=(z\sin\omega_1-n\omega_1)-\frac{z\sin\omega_1}{2!}\sigma^2-\frac{n}{3!}\sigma^3+\frac{z\sin\omega_1}{4!}\sigma^4, \quad . \quad . \quad . \quad (22)$$

if we include four terms of equation (3). If we put

$$\frac{z\sin\omega_1}{2!}\sigma^2=y^2,$$

the approximate value of the function (21) is given by

$$J_n(z)=\frac{1}{\pi}\sqrt{\frac{2}{z\sin\omega_1}}\int_{-y_1}^{y_2} dy \cos\{\phi_1-y^2-\alpha y^3+\beta y^4\}, \quad (23)$$

where $\phi_1=(z\sin\omega_1-n\omega_1)$,

$$\alpha=\frac{n}{6}\left(\frac{2}{z\sin\omega_1}\right)^{3/2}; \quad \beta=\frac{1}{6z\sin\omega_1};$$

and the values y_1, y_2 corresponding to points of inflexion on the auxiliary phase-curve are given by

$$y_1=\sqrt{z\sin\omega_1}-\frac{n}{\sqrt{2z\sin\omega_1}} \quad \text{and}$$

$$y_2=\sqrt{z\sin\omega_1}+\frac{n}{\sqrt{2z\sin\omega_1}}. \quad . \quad (24)$$

* Scientific Papers, vol. v. p. 620.

Since z is large the effective range of integration is large, but the terms αy^3, βy^4, only become appreciable compared with y^2 near the limits of integration. If we expand the cos term and omit the odd term containing the sines, as its integration from $-\infty$ to $+\infty$ is zero, we have

$$J_n(z)=\frac{1}{\pi}\sqrt{\frac{2}{z\sin\omega_1}}\int_{-y_1}^{y_2}dy\cos\{\phi_1-y^2+\beta y^4\}\cos\alpha y^3. \quad (25)$$

Approximate results are obtained by expanding $\cos\beta y^4$, $\sin\beta y^4$, $\cos\alpha y^3$ in series after expanding the $\cos\{\phi_1-y_2+\beta y^4\}$, and by making use of the integrals

$$\left.\begin{aligned}
\int_{-\infty}^{+\infty}dy\cos y^2 &= \sqrt{\frac{\pi}{2}}=\int_{-\infty}^{+\infty}dy\sin y^2,\\
\int_{-\infty}^{+\infty}dy\,y^4\cos y^2&=-\frac{3.1}{2.2}\sqrt{\frac{\pi}{2}}^{*}=\int_{-\infty}^{+\infty}dy\,y^4\sin y^2,\\
\int_{-\infty}^{+\infty}dy\,y^8\cos y^2&=\frac{7.5.3.1}{2.2.2.2}\sqrt{\frac{\pi}{2}}^{*}=\int_{-\infty}^{+\infty}dy\,y^8\sin y^2.
\end{aligned}\right\} \quad (26)$$

The result obtained in this way is

$$J_n(z)=\sqrt{\frac{2}{\pi z\sin\omega_1}}\left[\cos\left(\phi_1-\frac{\pi}{4}\right)\left\{1-\frac{7.5.3.1}{2^4}\cdot\frac{\beta^2}{2}+\text{etc.}\right\}+\sin\left(\phi_1-\frac{\pi}{4}\right)\left\{\frac{3.1}{2^2}\beta-\text{etc.}\right\}\right]. \quad (27)$$

* These integrals are regarded as divergent integrals. By integrating by parts twice we readily obtain

$$\int_{-\alpha}^{+\alpha}y^4\cos y^2dy=\alpha^3\sin\alpha^2+\frac{3}{2}\cdot\frac{1}{2}\cdot 2\alpha\sin\alpha^2-\frac{3}{2}\cdot\frac{1}{2}\cdot\int_{-\alpha}^{+\alpha}\cos y^2dy.$$

Let α now become infinitely great. The integrated terms $\alpha^3\sin\alpha^2$, and $\alpha\sin\alpha^2$, oscillate in value rapidly as α is increased, while the third term is a convergent integral. The results employed above are obtained by neglecting the oscillatory terms, and by taking the convergent integral to be the value to be assigned as a mean value of the required integral when α becomes infinite. The above cases are very similar to that of the Fourier integral in equation (1) of this paper: for α finite,

$$\int_0^{\alpha}\cos kx\,dk=\frac{\sin\alpha x}{x},$$

and when α is infinite, the integral has the value zero at all points except at $x=0$. The process of evaluation employed gives the correct values for the above integrals required in physical problems, and for integrals of the type contained in equation (1), several cases of which have been examined.

The expression given in (27) is in agreement with the well-known asymptotic expression except in the term containing β^2. To bring the final term of (27) into complete agreement with the corresponding term of the asymptotic expression for $J_n(z)$, the auxiliary phase-curve must be modified by the addition of the term $\frac{z \sin \omega_1}{6!}\sigma^6$. When this term is included, we obtain by the above method an expression which is correct as far as the term containing $\frac{1}{z^{5/2}}$; and the higher terms are obtained correctly when a sufficient number of terms are employed in the auxiliary phase-curve.

Applications of the expressions contained in the present paper occur in the problem of determining the front of a group of waves advancing in shallow water, and in connexion with the minimum of the group-velocity in the case of waves governed by gravity and surface-tension combined. The theory also allows of an extension of the well-known solution of the ship-waves problem whereby the motion in the neighbourhood of the line of cusps can be determined with greater accuracy. There is also the question of energy propagation in wave-motion in the cases to which the theory given in the present paper is applicable. These problems are of interest in themselves and also on account of their bearing on analogous problems of wave-motion in dispersive media; they will be dealt with separately in later papers.

CXXII. *The Movements of the Earth's Surface Crust.* *By* J. Joly, *Sc.D., F.R.S., F.T.C.D.**

Introduction.

IT is well known that periodically the Ocean floods the lower land-surfaces of the earth, and that such transgressional seas prevail for so long a time that geosynclines receiving the sediments washed from some mountain range may accumulate debris to the depth of many miles.

But still more strikingly eloquent of vertical movements affecting the continents is the fact that the mountains themselves are mainly built of marine sediments, although batholiths and other igneous bodies exist within.

The mountains clearly reveal the effects both of horizontal and vertical movements in the form of folding, overthrusting, block-faulting, etc.

* Communicated by the Author.

Furthermore, it is known that great mountain ranges now existing on the Globe received a remarkable increase of elevation during comparatively recent times; that these events were (geologically speaking) of simultaneous occurrence over the earth: and that wide-spread flooding of the land areas, with marginal and central transgressional seas, heralded these movements.

Looking back into the past we find over and over again evidence of similar events and always in the following sequential order:—(*a*) Prolonged crustal disturbances leading to fluctuating transgressions; (*b*) Greater and more permanent transgressions and, often, much local accumulation of sediments; (*c*) Mountain elevation and retreat of the continental seas; (*d*) Final great elevation of the mountain ranges and restoration of former continental levels. Attending these movements of the earth's crust volcanoes may break out on a great scale and vast floods of lava may escape at low levels, especially along the western margins of the continents or to the west of high mountain ranges.

The events which heralded the great "revolution" of Laramide times in N. America, and their final consummation in the elevation of the Laramide ranges, may well illustrate this succession of crustal movements. And, again, very many millions of years earlier—in Permian times—similar phenomena affected the same continent when the Appalachian ranges originated. Earlier still, near the close of the Pre-Cambrian and, finally, away back in the Archæan, one or two revolutions of extreme intensity and very long duration appear to have affected, to the point of complete transformation, the entire land-surfaces of the Globe.

Between these events, which seem to be cyclical in recurrence, lesser disturbances affected the crust—disturbances eloquent of unstable conditions and of some source of restless energy existing beneath.

Now, in this present paper I venture on an endeavour to trace the origin and inter-relation of these various events to:—(1) The existence of a general basaltic magma-ocean or isostatic layer in which the continents float and upon which the oceans rest; (2) The presence of a certain amount of radioactive materials throughout this magma-ocean; (3) The maintenance, both in the past and in the present, of isostatic equilibrium of the land-masses; (4) Certain forces acting on the earth's surface materials, forces of astronomical origin: *i. e.* tidal and precessional.

We shall first consider the existence and nature of the magma-ocean.

Existence and Nature of the Magmatic Layer.

The evidence for the existence of such a layer extending beneath the continents and oceans primarily arises from the support which the theory of isostasy has received in recent years. No one who has followed the evidence can question the fact of continental flotation and of the existence of downward extending "compensations" buoying up the greater raised features of the earth. These facts involve a sustaining, sub-continental layer. That this layer must be composed of material denser than the average continental rocks is evident. We have further guidance as to its nature in the great outpourings of basaltic lava at intervals in the earth's history, dating back to most remote times; and, again, in the fact that by far the greater number of the volcanoes of the Globe emit basalt. Yet another fact points to this rock-substance as composing the magma-ocean—its relatively low melting-point. Plainly the sustaining ocean must be of lower melting-point than the average continental rocks. The melting-point of the latter varies from 1400° C. to 1700° C.; the melting-point of basalt is below 1200° C. under like conditions of pressure.

The view that basalt composes the isostatic layer is supported by many petrologists. Notably, Daly ('Igneous Rocks and their Origin,' 1914), dealing with the problems of magmatic differentiation, volcanicity, etc., thus summarizes his conclusions:—"The facts of Volcanic Geology seem, therefore, to co-operate with the facts of plutonic geology in showing that the essential process in igneous actions on this planet is the rise of basaltic magma from the universal substratum along abyssal fissures" (p. 303).

The depth of the layer required by the theory of isostasy is not closely determinable. Some of the best authorities consider the most probable depth to lie between 60 and 70 miles.

Thus we perceive that basalt is the most prevalent and most important rock-material of the outer part of the Globe.

Melting of the Magma.

All basalts so far examined reveal small quantities of radioactive materials, both of the Uranium and Thorium families of elements. There are quantitative variations—relatively fairly considerable—but always actually concerned

with minute amounts, as the following table will show * :—

	Ra. grm. per grm. $\times 10^{-12}$.	Thorium grm. per grm. $\times 10^{-5}$.
11 Basalts (chiefly Hebridean)	0·5	0·38
5 Gabbros and Norites	1·3	0·50
8 Diabases and Dolerites	1·0	0·22
14 Basalts and Melaphyres (chiefly Deccan and Antarctic)	2·0	0·84
18 Basalts (generally representative)	1·4	0·63

It is well known that radioactive substances generate heat at a constant rate which no extremes of pressure or temperature hitherto tried affect or modify in the smallest degree. It may, therefore, be assumed with certainty that, *if the conditions prevailing in the magna are such that this heat is conserved, ultimate fusion of the whole mass is inevitable.* It must be kept in mind that this ceaseless generation of thermal energy progresses in every gram, in every cubic centimetre, throughout the whole body of the material.

The physical conditions otherwise affecting the magma are not everywhere the same; the pressure, of course, increases all the way down, and this will influence the melting-point, latent heat, and thermal expansion, as will be referred to again further on. When, therefore, we ask the question as to how far would attainment of the state of fluidity be a simultaneous phenomenon, we must answer with respect to the upper regions only; and always bear in mind that the word "simultaneous" is taken in its geological sense.

If we assume that at some stage in the history of the magma it is at its melting-point but in a state of quasi-solidity, lacking the latent heat necessary to produce liquefaction; then after a certain period the several constituent parts, differing in their radioactive content, melt in the order of their radioactivity, the richest melting first.

Now, in a region of the magma where the main body is still solid, nothing can come of such local fusion save that these more radioactive centres share their accumulated heat with surrounding basalts, causing them to melt and bringing about thereby intermingling with the poorer magma. Unless the heterogeneity of the magma with respect to radioactive constituents be on a very great scale (which we have no reason to believe is the case) this must be true.

* J. H. J. Poole, "The Average Thorium Content of the Earth's Crust," Phil. Mag. Apr. 1915; J. Joly, "The Radioactivity of Terrestrial Surface Materials," Phil. Mag. Oct. 1912.

This gradual, part-by-part, liquefaction of the magma must persist over a very long period. It represents the period of preparation for a great revolution. Volume changes (to be considered presently) are locally produced which may be of sufficient magnitude to affect restricted areas at the surface. The condition of change must continue until there is a final and general breakdown of the residual "rigid" ground-mass of the magma. When this occurs, and only then, the climax of a revolution is reached. Thereafter convective circulation on a big scale begins and the slow thermal flux permitted by the conductivity of the medium gives place to active circulation—melting and stoping of such surface-layers as may yet have escaped fusion and the convective distribution downwards of the cooled and denser magma which results.

We notice that in this sharing of heat among the constituent parts of the magma—the richer magmas melting down the poorer—it follows that neither the richest nor yet the poorest lavas determine the duration of the period required for the thermal accumulation to reach that critical amount which determines general fusion, but the average. A little consideration, in fact, shows that the extremes cannot control the date of the final breakdown.

Hence, in our time-estimates we take the mean values of the quantities of radium and thorium contained in the basalts (and their equivalents) as giving the best clue to the time-intervals which must separate world-wide revolution. For, as will be seen later, our assumption is that it is the volume-changes arising in the liquefaction of the abyssal magma which determine the most conspicuous events then taking place at the surface.

Now the radium content of a composite powder made up of 18 representative basalts *—as determined by the fusion method—and the thorium content as determined by the continuous-ebullition method (Phil. Mag. July 1911 and May 1919) are respectively—as cited above—$1{\cdot}4 \times 10^{-12}$ and $0{\cdot}60 \times 10^{-5}$ gram per gram. The heat continually evolved by one gram of radium in equilibrium with its related elements is $5{\cdot}6 \times 10^{-2}$ gram-calorie per second. The heat evolved by one gram of thorium and related elements is $6{\cdot}6 \times 10^{-9}$ calorie per second, as determined by Pegram and Webb (Phys. Rev. xxvii. 1908), which is somewhat lower than the calculated theoretical amount (Rutherford, 'Radioactive Substances and their Radiations,' p. 583 (1913)).

* These include 3 Hebridean, 4 Antarctic, 3 Deccan, and basalts from the Eifel, Saxony, Hessen, Siebengebirge, St. Helena, etc.

From these data we find that $11{\cdot}8 \times 10^{-14}$ calorie is generated per second in a gram of the rock, or 3·71 calories in one million years. In 25 million years 92·75 calories accumulate in every gram. If we accept for the radium content of the average basalt $1{\cdot}2 \times 10^{-12}$ gram per gram, we find that it takes 28 million years to accumulate 92·4 cals. per gram. According to Vogt (*Christiania Vid. Selsk. Skrifter*, 1904, p. 54 *et seq.*), the latent heat of such rocks may be taken as 90 calories. So also the experiments of Hempel and Heraeus (*Zeit. f. Elektrochemie*, 1903, p. 43) give the latent heat of fusion of Melilite (a substance somewhat analogous to basalt in chemical composition) as 90 gram-calories. Doelter (*Phys. Chem. Mineralogie*, p. 101) states that the latent heats of fusion of silicates are mostly around 100 gram-calories per gram.

We conclude that the latent heat required to liquefy 1 gram of average basalt at its melting-point would take about 30 million years to accumulate.

Volume-Change of the Magma.

The effects of pressure in modifying this conclusion are not definitely known. The melting-point rises with pressure. Vogt (*loc. cit.* p. 210) concludes that the pressure due to 25 miles of rock would raise the melting-point 50° C. Tamman gives reasons for believing that the positive volume-change, $V_1 - V_2$, becomes negative under very high pressure and consequently from the thermodynamical relation between melting-point, pressure, and volume-change, the melting-point will reach a maximum with increase of pressure and will then fall. Such a pressure as would prevail at a depth of 150 kilometres would give rise to the maximum melting-point (Vogt, *loc. cit.* p. 208). On this basis the melting-point continues to rise all the way down to the base of the magma-layer if the layer be such as isostasy requires. The whole matter is complicated by the effects of occluded gaseous matter, which seems to reduce viscosity and to confer considerable expansive force under decreasing pressure, *i. e.* attending vertical circulation.

However, as will be seen later, when fusion at length occurs in the upper parts of the magma certain tidal disturbances must arise. Currents to feed the tidal wave must originate, and these must grow in importance as melting progresses and the tidal effects augment. Such disturbances must be transmitted downwards, and even the lowest layers may be affected. It seems, therefore, probable that, when

melting becomes general above, there must arise ascensional movements wherever the conditions of viscosity permit. As matter of observation, at a very little over the melting-point basalt is an extremely mobile fluid.

There is another probable effect that must be borne in mind—supplies of heat from yet deeper regions of the earth may affect the lower layers. This is, in fact, certain, unless the earth be, for some reason, radium-free below some 70 or 80 miles down—obviously a most improbable condition. This is an added reason for the view that, when tidal effects set in above, grave disturbances may be transmitted far down and may bring up super-heated magma possessing great expansive properties due to its temperature and to juvenile gases. Daly (*loc. cit.*), in connexion with magmatic stoping by abyssal injection, has discussed similar problems.

Effects of the Volume-Change.

Now, the effects of general expansion will be to enlarge by a little the earth's radius. Both continents and ocean-floor will be upraised together. But change of density in those layers of the magma principally buoying up the continents will give rise to another effect. For, whereas the oceans are not floating by displacement, the continents are. Thus a general increase in the volume of the magma will raise both together, but the attendant change of density will cause the continents to sink. The result of this effect at the surface will be transgression of the sea upon the land.

It is difficult to give numerical estimates of the magnitude of this effect. The experiments of Day, Sosman, and Hostetter (Am. Journal of Science, Jan. 1914) seem in many respects the best we have. The volume-change attending fusion is sudden and amounts to 10 per cent. of the volume of the unmelted solid at its melting-point—or 12 per cent. of the volume of the crystallized basalt at or near the melting-point. There is a sudden and marked liberation of heat attending the change to the solid crystalline state. This is a restoration of heat from the latent to the sensible state. Its amount was not measured.

We cannot apply these figures directly to estimates of continental sinking and oceanic transgression, for the reason that it is improbable that the whole continental compensation is affected by it. This much may, however, safely be affirmed :—*The observed volume-change of basalt in changing state appears to be fully adequate to account for the most extreme transgressions revealed in past geological records.*

Cooling of the Magma.

Now, it may take some 25 or 30 millions of years to effect such a storage of heat as will result in a general change of state.

When, finally, fluidity is attained convective circulation begins, and cooling will be rapid. But while such rapid cooling will progress beneath the ocean floor, there will be then and at all other times, relatively little cooling immediately beneath the land-masses. We may take this last point first.

The fact is easily demonstrated. From their proper radioactivity and probable thickness the continental masses must possess basal temperatures approximating to that of the underlying basalt. In other words, both now and at any other time the gradient of temperature prevailing in the earth's continental crust is mainly due to the generation of radioactive heat within its own materials, and not in any notable degree to heat flowing up from subcrustal sources.

For suppose the continents to average 24 kilometres (15 miles) in thickness. Throughout this depth we infer from measurements applied to representative rocks that there is $2{\cdot}2 \times 10^{-12}$ gram radium and $1{\cdot}6 \times 10^{-5}$ gram thorium in each gram of rock (Phil. Mag. Oct. 1912 and Apl. 1915). The thermal output from these quantities of radioactive elements is $22{\cdot}8 \times 10^{-14}$ cal. per second. On a specific gravity of 2·7 this works out as $1{\cdot}5 \times 10^{-6}$ cal. per second for a volume 1 square cm. in cross-section and 24 kilometres deep. But the heat escaping at the surface, as calculated from a gradient of 1° C. in 32 metres and a conductivity of 0·005, is $1{\cdot}6 \times 10^{-6}$ calorie per second.

Thus, practically all the heat escaping at the surface of the continents has been generated within the rocks of which it is composed, and therefore cannot come from beneath. It follows that the radioactive heat generated immediately beneath the continents is at the present time being conserved—the floating land-masses acting as an adiathermenous layer to the underlying magma at or near the melting-point of the basalt.

However, although this, very probably, involves the local persistence of molten basalt beneath the crust, there must be considerable lateral circulation when consolidation is in progress beneath the oceans. For the loss of volume attending cooling must draw on the sub-continental magma to a considerable extent. There is also movement due to tidal effects, as already pointed out. If these effects result in the upper

parts of the magma shifting with reference to the deeper layers (as will, later, be referred to), this must give rise to horizontal shearing at all levels, and in this way sub-continental cooling and solidification will be promoted. When solidification is attained these tidal movements probably cease, or almost cease.

But the conditions of heat storage and heat loss beneath the oceans are in many respects different. There appear to be reasons for believing that not only will the conditions there prevailing lead to effective conservation of most of the energy during times of thermal accumulation, but also will favour its more rapid escape in times of revolution.

There is high probability, almost certainty, that the ocean floor is itself composed of basalt. The reason for this view is the fact that gravity measurements appear to show that the lesser density of the ocean is compensated by excess of mass beneath. In fact, the view has been advanced that the oceans are where they are because of this excess of mass. Again, the oceanic islands and volcanoes are strikingly basaltic in character.

But if composed of basalt then is the ocean floor exposed to fusion and stoping by rising currents of molten magma. The amount by which its thickness is reduced while it is borne upwards on the molten and expanding magma we do not know. But it is possible to arrive at some idea of what the initial thickness of the ocean floor may be before it is attacked by the liquefied lava beneath. By the "floor" is meant that topmost layer of the basaltic magma which falls in temperature below the melting-point.

The problem is similar to that solved by Lord Kelvin with respect to the downward distribution of temperature in a globe cooling from fusion by the passage outward of heat to an environment maintained at a constant low temperature. Kelvin's value for the diffusivity is inapplicable to the present problem, for it is, in fact, based on a mean experimental value obtained on substances only one of which (that on "the trap rock of Carlton Hill") is applicable to the present case. Correcting for this we next assume that the magma is everywhere solid in the sense that it loses heat by conductivity only, but is near its melting-point. The surface is maintained at 0° C. by the waters of the ocean. If, now 25×10^6 years are available for the growth of the sub-oceanic floor, we seek to find the distribution of temperature at the expiry of that period and the thickness of the floor—that is, the distance from the surface at which the temperature approximates to 1150° C. We find that

at 32 kilometres (20 miles), the temperature is nearly 1100° C.

In reaching this result we have, for purposes of simplification, neglected (*a*) the development of radioactive heat within the cooling layer; (*b*) the increased value of the thermal capacity of the basalt at high temperatures. According to Roberts-Austin and Rucker, Barus, and others (Vogt, *loc. cit.* p. 40) this varies from 0·180 at 20° to 0·285 at 1100°; (*c*) change in the conductivity at high temperatures. H. Poole has found no variation up to 600° (Phil. Mag. Jan. 1914); but it is probable that at higher temperatures it will diminish. The effects of these variations will be to sharpen the gradient, decreasing the thickness of the layer. (*b*) must reduce it by some 15 to 20 per cent. and (*a*) at least as much again. The probable value would be about 15 miles.

This result—which, for want of the sufficient data, is an approximation only and may be excessive by 3 or 4 miles—enables us to conclude that during the inter-revolutionary period the cooling by conductivity will give rise to a gradient of temperature downwards, rising to the magmatic temperature at a depth of about 15 miles. This is the probable thickness of the ocean floor.

[It supports the view that below a certain depth, comparable with the thickness of the continental crust, there is complete conservation of radioactive heat throughout the period separating the great revolutions.]

These considerations give some clue to the conditions which may control the upward passage and escape of heat through the ocean floor, as estimated above, when the conserved heat beneath has accumulated to the point of bringing in a period of revolution.

It is evident that, when the magma beneath the ocean floor has become fluid and circulatory movements begin, the floor which covers in the magma is, at its base, at the temperature of the magma, and in its lower parts only requires the necessary latent heat to again revert to the fluid state. It will be, therefore, rapidly melted away. Neglecting the possible intensification of these effects arising from superheated lava rising from beneath, and assuming the entire layer to possess the melting-point of the upper stratum of lava, there must be rapid (geologically speaking) thinning of the sub-oceanic floor. It is quite possible that this thins out to an extent enabling the greater part of the stored latent heat to escape in a very few million years and before the floor is completely removed. Much heat will doubtless be lost by

igneous eruptions through the floor. But, again, neglecting such aid, it is easy to show that an ocean floor reduced to some two or three miles in thickness would permit of such a heat loss as would confer the quasi-rigidity and the density of the solid state upon the greater part of the magma, not only beneath the oceans, but beneath the continents.

An extreme case is to assume that *all* the latent heat of the entire magma has to escape through the ocean floor. Even were this the case, a floor 2 miles thick, possessing the conductivity 4×10^{-3}, would pass out all this heat in 8 million years, and, of course, one-half of this thickness would dispose of it in 4 million years. In point of fact, the escape in this manner of *all* latent heat would be impossible; because the circulation must cease when a certain fraction has become solid—sufficient to diminish tidal activity and to check convective movements.

Effects of the Cooling of the Magma.

We may now return to a consideration of the surface-effects referable to the changes progressing in the magma.

We saw that melting of the magma produced continental sinking and transgression of the sea upon the land. This we now refer to the conservation of radioactive heat within the magma under the conditions we have described. But we have also traced a source of rapid loss of heat and re-solidification of the magma. The surface-effects of this must evidently be the restoration of former continental levels with reference to the oceans. For, while both continents and oceans will be affected by the change in such a way as to move downwards, the buoyant effect on the continents must be such that these must rise relatively to the sea-level. Hence, transgressional seas will disappear off the land-areas.

The upward movement will more especially prevail where deep compensations exist. Such an up-lift as the worn-down Appalachians experienced in late Cretaceous times, or the vertical movements which affected the Andes in more recent times, doubtless originated in this manner. Mountain-building movements are, probably, largely referable to this density-change which sets in towards the close of a great revolution, as will presently be more fully explained.

The Time required for a Revolution.

It will be gathered from what has now been said that to the isostatic layer and its thermal fluctuations (arising cyclically from storage of radioactive heat to the point of

liquefaction of the layer), on the present theory, the vertical movements of the land are to be referred. And we have seen that the time intervals which, on our rough computation, we have arrived at are not inconsistent with estimates of geological time.

It would seem that four or five periods of major revolution can be recognized since Algonkian times, although geologists do not seem to be in perfect agreement as to the number of revolutions which are to be regarded as of world-wide significance.

It is inferred by many that the Palæozoic was preceded by such an event. Some American geologists call this the Grand Cañon Revolution. A second revolution is recorded in the Silurian and Devonian rocks:—the Caledonian Revolution. A third occurred in Permian times, known as the Appalachian. A fourth culminated late in the Cretaceous and early Tertiary, which was responsible for the major development of the Cordilleras of N. and S. America and in America known as the Laramide Revolution. A fifth ushered in our own times and is responsible for the principal development of the great Eurasian chains. It is known as the Alpine Revolution.

Now, these developments involve four periods of genesis comprised within what is called "The age of the earth." They are, therefore, on the lower estimates of this interval comprised within some 170 to 200 millions of years at most. The preparation for the Pre-Cambrian revolution probably extended back into more remote times. Thus some 40 or possibly 50 millions of years are required for the preparation, development, climax, and decadence of a great revolution. According to the view of some, far longer periods would be involved.

The Lateral Movements.

But the phenomena attending vertical movements of the land relative to the ocean are not the only cyclical events in geological history which call for explanation. For, as we have seen, attending these vertical movements we find evidence of lateral thrusting in the folding and horizontal dislocation of the rocks. The sources of vertical movements and of horizontal compression are, plainly, genetically connected. Of this there is no doubt, for all over the world the order and inter-relation of the events seems to have been the same; the greatest display of orogenic activity appearing towards the close of a great revolution and after transgressional seas have largely disappeared.

Now, there two sources to which lateral movements may be referred and which arise out of the physical changes experienced by the isostatic layer. Both these sources appear to be, in some degree, inevitable, and therefore are *veræ causæ*, so that we conclude that both must have operated.

Mountain-building.

But before considering them it seems desirable to discuss for a little what the structural features of mountains actually reveal. Vertical movements are certainly demonstrated and often on a very great scale. The interest of the matter arises in the part played by horizontal movements. One eminent authority on isostasy—W. Bowie—considers that much of the rupture and distortion of strata, ascribed formerly to regional forces acting horizontally, are accounted for by vertical movements ("The Earth's Crust and Isostasy," 'The Geographical Review,' Oct. 1922). Horizontal movements have certainly contributed to mountain structure. Whether they play any direct part in the elevation of the mountain is another matter.

Going back to the loaded geosyncline, it is certain that this is a region of diminished rigidity within the continental crust. For the depression determined by isostasy exposes it to higher temperatures than prevail in the normal crust. The phenomena of regional metamorphism testify to the intensity of thermal conditions. Fusion may not be brought about (the melting-point of the floating continental crust is, as we have seen, from 200° to 500° higher than the m.p. of basalt), but rigidity may be so far diminished that comparatively small forces may give rise to the folding of strata.

Beyond the production of this lateral folding, there may be little more ascribable to horizontal forces. For, in fact, if the conditions of isostatic adjustment prevail throughout the genesis, vertical movements must be almost entirely due to buoyancy forces arising in the changing density of the magma.

We have to remember that, while the horizontal forces are in operation, the magma beneath is at its lowest density. At that period there is, in fact, very little difference in specific gravity between the continental materials and the melted substratum. It is therefore impossible that in this stage lofty vertical elevation could be attained. The compressed strata must go down and not up, and their downward displacement involves very little expenditure of energy. The

rise above the continental surface will be insignificant. The conception, therefore, that chains such as the Alps and Andes were forced upwards by lateral forces cannot be correct. The upward movements, according to the present theory, came later, when the heat-loss restored the higher magmatic density. Then the energy of upheaval is referable simply to the gravitational potential of a general raised magmatic surface over the earth. This falls a little when the mountain ascends. The effect is purely hydrostatic.

The Geologist is not, therefore, required to adduce horizontal forces of great intensity, but he must account for movements adequate to shorten, perhaps by a score of miles, the width of a sedimentary area. If the over-thrusting in the Alps has been correctly estimated, movements of twice or three times this magnitude call for explanation.

Lateral Forces arising from Change of Area of Ocean Floor.

We now return to the sources of mountain-building forces which arise from the changing physical state of the magma. Looking back to earlier stages of our argument, we find that the liquefaction of the isostatic layer involves an increase of the earth's mean radius. Taking the depth of the magma to be 70 miles and that at the height of a revolution it experiences an average volume-expansion of 10 per cent., we arrive at the following figures. The primary mean radius of the Earth is 3963·2 miles (its present value). This corresponds to an area of 197,380,000 square miles. The volume of the magma is obtained from this after deducting the displacement of the continents. Taking the area of the continents as $52{\cdot}5 \times 10^6$ sq. miles and their immersion as 15 miles, the magma-volume comes out as 13×10^9 cubic miles. The increase of 10 per cent. is therefore $1{\cdot}3 \times 10^9$ cubic miles, and the corresponding increase of the earth's radius turns out to be 6·5 miles—which involves an aerial increase of 650,000 square miles.

Now, this increase must fall upon the oceanic areas, because the continents are homogeneous and, in fact, are floating upon the expanding magma. The ocean floor is at this period being reduced greatly in thickness, due to the hot circulating lava. It must now break up under the expansive forces. It is rent by cracks, which again are filled in by abyssal injection, and before any considerable cooling has come about we must suppose that a larger ocean by some 650,000 square miles has come into existence, floored by a corresponding basaltic floor of a thickness which may be from 5 to 10 miles; possibly more; possibly less.

The increased surface-area of the earth arrived at above corresponds to a circumferential increase of 41 miles. This, also, necessarily falling upon the oceans means that the equatorial span of the Pacific will increase by 30 miles, and that of the Atlantic by 11 miles.

Attending the surface-solidification of the magma, the downward movement of the ocean floor gradually begins and the continents become pressed-upon, on every side, by the enlarged and strengthened oceanic floors. Even if buckling of the floor results the lateral pressure must continue, for the rigidity of the cooled basalt is considerable. This effect will give rise, pre-eminently, to very intense horizontal thrusts (although of limited range) on the continental land-masses. The pressure must long continue and may be adequate to find out the weak places of the land and to fold and shear the sediments in the upper few miles of the geosynclinal accumulations, seconding the intervention of other forces to be presently discussed.

As regards the estimated magnitude of this expansional effect, the amount of the volumnar expansion assumed is, to some extent, arbitrary. The upper part of the magma may, indeed, enlarge or contract by some 10 per cent. of its volume in changing from solid to liquid and *vice versa*. The volumnar change of the deeper parts is unknown, but if—as appears probable—there is vertical circulation of super-heated material, the volume-change may be considerable. The assumption of a mean change of 10 per cent. may, however, be somewhat excessive.

It is noteworthy that the amount of attendant change in the magnitude of the ocean floor is in no degree affected by thermal expansion or contraction of the floor itself. For, in point of fact, the mean temperature of this crust is unchangeable, its upper and lower surfaces maintaining unchanging temperatures—*i. e.* controlled above by the ocean of water and beneath by the melting-point of the ocean of basalt.

Upon the question as to the adequacy of such movements as might arise from this source, it is to be observed that they are repetitional with each revolution. Thus the total horizontal contraction involved in the Rocky Mountains has been estimated at 25 miles east to west. But this range was mainly created in Laramide times. It was again further acted upon in Pliocene times. The latter disturbances chiefly took the form of vertical uplift. But, as we have seen, there is no vertical uplift without previous downward displacement into the isostatic layer. The downward displacement may be due to geosynclinal loading alone or to

loading subsequently disturbed by lateral forces. It seems, therefore, probable that lateral forces, acting during two successive revolutions, were responsible for the Rocky Mountains as we see them.

Accompanying the volume-changes of the isostatic layer there would arise a small effect upon the rotational velocity of the Earth. The retardation attending expansion of the magma and increase of the Earth's radius would be temporary, however—the original velocity being restored upon the shrinkage of the magma. It does not appear that this temporary effect would in any appreciable degree affect the changes we have been discussing.

The Inter-revolutionary Disturbances of the Crust.

But, in addition to the major movements attending world-wide revolutions, there are minor ones—often not inconsiderable, however,—which appear to occur at irregular intervals and which involve not only a certain amount of transgressional flooding but also orogenic movements in a horizontal direction.

I think we may refer these disturbances largely to conditions similar to those we have been considering. For, while we have dwelt upon the broad features of magmatic changes over geological time, it is impossible to maintain that more local thermal fluctuations at irregular times have not occurred (*ante*, p. 1171). The floating land must, in fact, be continually subjected to the effects of changing buoyancy. This was especially noteworthy in the geological history of the Pacific borderlands of North America. Transgressions and re-élevations were frequent events. But the forces of uplift must have affected the adjacent ocean floor for many miles to the west, and the fractures induced by tensile stresses must always be repaired by abyssal injections. There is no other way. Attending downward movements, compressive forces must accordingly arise along the continental margin. This seems quite inevitable. The only question at issue is really one of the adequacy of such repetitional movements. This question we cannot answer. But such as they were these forces were many times repeated. Schuchert ('Text-book of Geology,' p. 979) estimates at least eight minor periods of crustal disturbance as having affected the continent of North America. Again, we must recognize the fact that local vertical movements of an oscillatory character affecting a continental interior cannot take place without engendering horizontal compressional

movements on the same mechanism as I have referred to above. In short, from the physical properties of rock towards tensile and compressive forces, and the ever-present existence of the abyssal magma beneath, ready to enlarge such cracks as may develop and infill them with rock-making materials, pulsatory vertical movements may account for much crustal distortion. Horizontal forces directed in any azimuth may be engendered in this way.

In the case of the greater world-wide movements when the rise and fall of the entire crust takes place the wider the oceanic reach the greater must be the orogenic effects. Here we recall the significant remark that the greatest mountain ranges face the widest oceans. There are no mountains around the Atlantic comparable with the Cordilleras. The Himalayan fold-mountains range perpendicularly to one of the greatest oceanic reaches of the Globe.

Effects of Tidal and Precessional Forces.

But other factors arising from the existence of a radio-active isostatic layer may enter into this question, and possibly upon a very effective scale. I mean precessional and tidal forces.

It is recognized in tidal theory that the tidal wave which is maintained on opposite faces of the Globe must act as a brake applied to the surface of the earth opposing its axial rotation. This brake, operating to retard the west-to-east motion of the earth's surface, may be expected to give rise to a motion of the whole outer crust of the earth with reference to the interior—that is, if viscous movement of the outer over the inner parts is possible. In this way the length of the day may not represent the real rate of rotation of the earth, which spins within the outer crust with slightly greater angular velocity. Darwin ('The Tides,' p. 276) looked to such effects acting, in earlier periods of the World's history, upon a viscous planet as possibly wrinkling the surface in such a manner as to mould the observed continental contours. Eddington ('Nature,' Jan. 6, 1923) considers it possible that purely oceanic tidal movements, brought to rest in land-locked areas, might have given rise to crust-wrinkling.

The tide generating force is intrinsically a feeble force at the present time. The horizontal tidal force is only one eleven-millionth part of the weight. In past times, according to the tidal theory of the Moon's history, the force

must have been far greater, the horizontal tidal force increasing inversely as the 6th power of the Moon's orbital radius.

According to the theory I have been discussing, at intervals in the world's past history there came into existence a sea of molten rock having a depth probably not less than twenty times that of the ocean and possessing three times the density of water. In its upper parts this lava-ocean was, probably, highly mobile—quite as mobile as water. My own observations (Trans. R. D. S. vi. p. 283), made some years ago, showed that basalt raised just above the full melting-point possesses much the same properties as a very "thin" oily fluid. Day and his colleagues (*loc. cit.*) record similar observations. The question arises, how far may tidal movements prevailing in such an ocean have contributed towards crustal disturbances in the past and how much would they be effective even in Pliocene times or in the future? Data as to the downward viscosity of the magma-ocean are not available, and doubtless they must be important factors in determining the answer to these questions.

But it seems allowable to infer that the effects of world-revolutions must have been to develop retardative forces acting on the outer crust of the earth much in excess of anything of the same kind due to the oceanic tides of our time.

Now, if any considerable retardative effects affected the surface-features of the earth—I mean the continents and oceans and the ocean floor—so as to withhold them from partaking of the full west-to-east angular velocity of the earth, this effect of tidal force would seem to involve local stresses on the more deeply immersed parts of the floating land-masses, which might be very considerable.

To understand this we must note that the retardative effect referred to must be effective chiefly in the upper regions of the magma ocean, for its lower layers, in contact with more rigid materials beneath and, owing to pressure, probably possessed of greater viscosity than the upper layers, must partake more nearly of the full angular velocity of the earth's rotation. It is easy to see that these conditions must give rise to a west-to-east drive or pressure of the heavy magma against the immersed parts of the continents. It must be remembered that this state arises at a time when the ocean floor has been reduced in thickness, so that the submerged western coasts of the continents are left exposed to the effects of differential movements in the magma. For, in fact, the horizontal tidal forces exert an east-to-west pull upon the continents, and this is resisted by the earth's

rotational energy transmitted through the medium of the molten magma.

These conditions involve differential effects upon the floating land-masses. For the more deeply compensated continental features experience the west-to-east magmatic drive more than shallower land-masses. And, again, turning or rotational forces would arise, due to those greater downward extending compensations which might be located excentrically respecting the resultant or centre of magmatic forces, or where continental masses extended partly into equatorial areas—the linear velocity of the magma being greatest at the equator. Such rotational effects may have affected mountain development. Comparatively small movements would suffice: thus, if the African continent and Peninsular India were, even to a small extent, affected in this way, by the more active equatorial currents upon their southern extension, much of the Eurasian folding would find explanation. We have seen that at the height of revolution the ocean floor is, probably, much disturbed as well as reduced in thickness, and its resistance thereby diminished.

The effects of these conditions on mountain-folding would, probably, be principally experienced where the geosynclines had forced the land deep into the magma. Here the east-going magmatic pressure would be largely concentrated and the temperature conditions also most severe; lateral folding and compression into still greater depths—the conditions being self-intensifying—being a very probable result. Even under pressures of no very great intensity per unit area, provided they were long continued, these results might be expected. The final buoyancy effect would ultimately force upwards, isostatically, the bent and folded masses—along with batholithic invasions of the basaltic magma. Thus the ranges raised above the general continental levels would be formed.

The Cordilleras of western America would seem to stand as a monument of the forces acting from west-to-east which we have been discussing. It may well be that, whereas both the west and east coasts of the Pacific owe to an expanded ocean floor the major wrinkling of the continental surface, the predominant orogenic phenomena displayed on the eastern coasts is due to a force which cannot have acted upon the western coasts—the magmatic pressure arising in horizontal tidal and precessional forces.

Schweydar (*Zeitschr. d. Ges. f. Erdk. zu Berlin*, 1921, S. 120–125) has investigated a precessional force, which tends to urge the continents westward, and which has, of course,

like the tides, an astronomical origin. From his statement it appears that this force must be considerably greater than the horizontal tidal force, and, obviously, its effects must greatly augment in times of revolution. It is strongest at the equator and is null at 36° N. and S. It must conspire with the tidal force to retard the west-to-east movement of the earth's crust. (See also Wegner, *Die Entstehung der Kontinente und Ozeane*, Berlin, 1922.)

It is significant as regards this probable intervention of tidal and precessional effects that the great lava-floods of geological history have welled up through fissures on the western sides of continental land or west of great mountain ranges, or, again, have appeared where rifts ranging north and south have been attended by deep crustal faulting and sinking. The Deccan basalt thickens towards the west, and western coastal fissures have been traced. The Hebridean basalt was poured out westward of a continent. The Disco basaltic flows appeared to west of the Greenland ranges. The western inter-montane regions of North America are largely flooded by basaltic outflows. The great African rift appears to have determined intense volcanism and basaltic outflows. The Christiana rift seems to be a similar case. The existence in revolutionary times of easterly basaltic pressure beneath would account for this remarkable localization of igneous activity.

Volcanic Activity and the Present Theory.

The present theory involves a probable decadence of volcanic activity in inter-revolutionary times. The existing explosive type of volcanism is, doubtless, a purely local phenomenon in many cases, the supply of thermal energy coming from deep-seated pockets of the molten rock. But volcanic activity may be associated with seismic indications of tectonic features, which seem to refer it to the activity of the general fluid substratum beneath the continents ; or of sub-oceanic supplies which at the present time lie beneath an ocean floor which is still undeveloped. Cases of volcanism of this type, of a remarkable character, are reported from Japan and elsewhere. The great lava-flows are, however, a feature of revolutionary conditions, which must on a great scale cease with the cessation of tidal movements. Still, phenomena of the sort might long survive, for sub-crustal reservoirs of the molten magma, if once enclosed by solid rock, would cool with secular slowness ; and any source of compression—such

as shrinkage of the containing rock or earth-movements—might bring it to the surface. The Icelandic eruptions of recent times may originate in this manner.

The higher volcanic cones do not appear to emit lava. Light ejectamenta—dust and steam—may be emitted. It is doubtful if, at their existing elevation, any definite lava-flows have taken place. Bonney ('Volcanoes,' p. 275) refers to this as a general feature of volcanism. The volcano outgrows its strength. The comparatively recent final elevation of the Andes may have operated in this way.

However, on the theory herein advocated, the lava-supply of volcanoes does not call for hydrostatic pressures extending into the depths. It is more probable that the lava-supply arises in laccoliths and such-like bodies which have been carried up with the general mountain elevation, and which for long ages are adequate to supply the comparatively small trickle which constitutes a volcanic eruption. As regards the fact that volcanoes emit magmas of various rock-clans, Daly has treated the matter so clearly and ably that it suffices to refer to 'Igneous Rocks and their Origin.' As stated above, there is no reason to suppose more than the one abyssal magma of basaltic composition.

Broadly viewed, volcanic and seismic phenomena are surviving memorials of past times, when the continents were exposed to vertical and lateral disturbances far greater than prevail to-day. The stored energy must be very great when integrated over large areas. It exists partly as uncompensated gravitational potential; partly as elastic potential, which can run down only by effecting structural readjustments. It is doled out age after age in the form of slow elevations and depressions, crumpling and faulting, in seismic and volcanic effects which in themselves are relatively local and petty phenomena. Denudation very often pulls the trigger in these cases.

The Dominance of Radioactivity.

Throughout the whole great matter we recognize in radioactivity a source of energy which has controlled the surface-history of the Globe. In the fusion and expansion of the isostatic layer the vertical movements are directly involved. When the mountains finally arise under isostatic forces the general magmatic level sinks a very little. Local movements of radioactive heat may control inter-revolutionary disturbance. Changes in the sub-oceanic floor may give

rise to lateral pressures. Again, radioactive heat prepares the way for tidal or precessional forces to intervene, and the surface of the earth becomes for the time being a brake applied to the rotating planet—a brake which absorbs some of the energy of rotation and for long ages afterwards exhibits the diastrophic effects.

The Question of Continental Drift.

The question of the possibility of continental movements having occurred in past times arises naturally in connexion with the foregoing views. The main point at issue, however, is one which we do not seem able to determine—how far, during times of revolution, the ocean floor may have been reduced in rigidity and thickness. For it is obviously hard to imagine that in times when a thick and rigid ocean floor binds the continents together—any forces with which we are acquainted can have attained such intensity as to rupture the connecting crust. However, during the height of a great revolution, under the operation of convective currents—probably in part superheated—assailing the basaltic ocean floor, almost anything may have happened so far as the stability of the floor is concerned. It may have been fractured or softened to an extent permitting of differential forces—already referred to as arising from tidal or precessional sources—to occasion slow drifting from west-to-east. For such must be the direction of continental movement relatively to the earth's surface.

Under such conditions Eurasia may have drifted from America in Laramide times. New Zealand, in virtue of its great loading of mountain ranges, may have parted from Australia; the Festoon Islands may have been carried eastward from Asia; Peninsular India may have parted from the African Continent; etc., etc.

But, as I have intended to convey, while the possibility of continental drift appears to be involved potentially in the present views, the former existence of all the necessary conditions does not seem to be demonstrable. Final support to the theory of continental drift must come from evidence which it is outside the scope of this paper to discuss.

CXXIII. *Notices respecting New Books.*

An Introduction to the Chemistry of Plant Products. Volume 2. *Metabolic Processes.* By P. Haas and T. G. Hill. London: Longmans, Green & Co. Price 7*s.* 6*d.*

THE present volume forms a sequel to the volume by the same writers 'On the Nature and Significance of the Commoner Organic Compounds of Plants,' which was recently published. The volume treats a series of the more important outstanding problems of the synthesis or the building-up by the plant of fats, carbohydrates and proteins, of respiration—the production of energy for the maintenance of the life of the plant, and growth—the balance between these constructive and destructive processes.

The authors have courageously put aside the task of giving a mere digest of the literature of the problems with which they deal, and the book is consequently more likely to inspire students ultimately to turn their attention to serious problems needing original treatment than the usual text-books. Their self-imposed task has been to describe the present position in the various problems under consideration, in order to make as plain as possible the outstanding difficulties, as well as to explain the methods by which the results already reached have been obtained.

In the section dealing with the problem of growth the preoccupation of the authors with the so-called "Compound Interest Law" is to be regretted. The exponential and logarithmic laws are but isolated examples of mathematical functions, and the prior probability of the growth-curves conforming to these laws is by no means large. Strong evidence of growth-curves agreeing with these curves is necessary before a reasonable probability for this hypothesis of growth can be established. A more illuminating treatment of this important and fundamental problem seems to require a freer use of mathematical functions. No structural problem in any branch of mathematical physics of the same order of importance has ever yet been solved by complete adherence to one type of solution, without reference to the general characters of the phenomena under discussion.

The experimental side of the problems under consideration is, on the whole, left on one side. It was plainly not necessary or desirable to burden the book with detailed discussion of points of purely experimental interest.

The Mathematical Theory of Relativity. By A. S. Eddington. Cambridge University Press. 20*s.* net.

The first draft of this book has been accessible for some little time in the form of a mathematical supplement to the French edition of the author's 'Space, Time and Gravitation.' This draft has now been developed into a more systematic and comprehensive treatise on the mathematical theory of relativity.

The author is concerned to work out deductively the whole theory from the premisses suggested by Einstein, and there is consequently no attempt at explaining in general terms the revolution of thought which the theories of relativity have initiated. With this subject matter the book must necessarily be mainly an exercise in mathematical deductions from highly abstract premisses.

The first section of the book gives a quasi-mathematical, quasi-philosophical introduction to the subject. It is much condensed, and needs to be read in connexion with the author's previous work, in which the point of view of this introduction is worked out *in extenso*.

The major part of the book deals with the theory of Tensors. It will be of great value to have in the present very clear and easily accessible form the body of tensor analysis as it is required for the development of relativity theory. The author's own generalization of Weyl is also included. Time alone will show how far this or any other attempt to link up relativity ideas with atomic structure and the Quantum theory will be successful.

Principles of Geometry. By H. F. Baker, Sc.D., F.R.S., Lowndean Professor of Astronomy and Geometry, and Fellow of St. John's College, in the University of Cambridge. Volume II. Plane Geometry, Conics, Circles, Non-Euclidean Geometry. Cambridge University Press: 1922. Price 15*s.* net.

Professor Baker gives plenty of good material in his second volume, but he makes it a little difficult to assimilate by not laying sufficient emphasis on the structure of his subject. His intention to be practical is perhaps carried out at the expense of obscuring to a certain extent the principles which it is his main object to expose.

As far as the experienced reader is concerned, this does not matter very much, as it is a comparatively simple matter for him to disentangle the principles from the details, which, indeed, illustrate the principles admirably. But it undoubtedly makes the book very difficult for one who is not in such a fortunate position.

The "symbols" which play such an important part in the book call for rather more explanation than appears to be given. They cannot be symbols in the ordinary sense because they are themselves symbolized; they are plainly logical constructs of some kind or other, and ought to be explained.

A great many readers will undoubtedly feel very grateful to Professor Baker for the way in which he has carried out the arduous task of expounding the principles of Geometry. The principles of Analysis are simple enough, for there is only one kind of analysis. But those of Geometry are another matter. There are many kinds of Geometry.

Synthetic Colouring Matters: Vat Colours. By Prof. J. F. Thorpe, F.R.S., and C. K. Ingold, D.Sc. Monographs on Industrial Chemistry. Edited by Sir Edward Thorpe. Pp. xv+491. London: Longmans, Green & Co. 1923. Price 16*s*.

The discovery of the constitution of Indigo led to the synthesis of a number of analogous coloured bodies, all of which like Indigo are insoluble in water; in order to employ these substances as dyes they have first of all to be converted into the colourless water-soluble leuco-compounds, which by subsequent oxidation produce the insoluble dye upon the fibre. This process, known in technical practice as vat dyeing, is essentially the same as has been practised by primitive races from time immemorial with Indigo. Since the commencement of the present century a large number of anthraquinone derivatives with similar tinctorial properties have been put upon the market, and the wide range of colour and fastness of these substances makes the vat dyes amongst the most valuable of all colouring matters. The present volume contains an account of the chemistry of these very numerous and intricate substances, the complexity of which is shown by a glance at their structural formulæ, which are given with lavish profusion throughout the book, and the specialist requiring information concerning the preparation of any particular member of the group will find a mass of information collected together within it pages. To the general reader, however, the first three chapters will especially appeal, since they contain an interesting historical survey of the subject of dyeing including such questions as the woad staining practised by the Ancient Britons and mentioned by Cæsar, and also the nature and origin of the Tyrian purple of the ancients.

It is to be regretted that the publishers have seen fit to have the book printed in Germany, but the cost of putting up the structural formulæ may well have been prohibitive in this country.

CXXIV. *Intelligence and Miscellaneous Articles.*

ELECTRIC FIELDS DUE TO THE MOTION OF CONSTANT ELECTROMAGNETIC SYSTEMS.

To the Editors of the Philosophical Magazine.

Gentlemen,—

In a footnote on page 1124 of the Philosophical Magazine for December 1922, Dr. S. J. Barnett, in referring to my paper "Unipolar Induction" (Physical Review, vol. xv. pp. 365–398, 1920), makes the following statement:—

"In connection with this experiment Swann, l. c. *ante*, has stated that Maxwell's equation (1) cannot be applied to the case

of rectilinear motion to show that the field is polar *because* (he states) *in this case the vector potential is not independent of the time.* This is clearly an error. Several examples of the contrary are given above, in addition to this particular case."

It is perhaps hardly necessary to do more than quote the statement in my paper to which Dr. Barnett refers to show that he has inadvertently misquoted me. The statement in question occurs on page 390 of my paper, and is as follows :—

"We cannot immediately import the ideas we have invoked in the case of uniform rotation to explain a shielding effect of the type referred to, because the vector potential is not independent of the time in the case of rectilinear motion ; so that it is not immediately obvious that the whole of the field E as given by (5) is derivable from an electrostatic potential."

I think that this statement can hardly be taken to imply that equation (5), which is Dr. Barnett's equation (1), cannot be used for the proof of the result in question, for the case under discussion, but only that the result does not follow *immediately* as it does for the case of rotation. In fact, it is implicitly on the basis of equation (5) that I prove the result in my paper ; and every expression for E in that paper is obtained directly or indirectly from this equation, whose truth is universal.

In so far as Dr. Barnett makes reference to other theorems, points of view, and discussions in my paper, I may say that it was not my intention to claim that these were entirely new, even though some of them might not have been published before. Indeed, I have always maintained that, from the standpoint of one who accepts the classical electrodynamics, none of the usual experiments concerned with moving lines of magnetic force present the slightest difficulty. It is only in extending the moving-line theory to forms inconsistent with classical electrodynamics that difficulty is encountered. To discard the conception of moving lines entirely would be unwise, since it certainly gives correct results in the most important cases, so one of the main objects of my paper was to formulate the exact sense in which the moving-line theory must be used if it is to lead to results consistent with classical electrodynamics. A sufficiently large number of experiments claiming to demonstrate difficulties in electromagnetic theory, and involving arguments concerning moving lines of force have appeared, even within recent years, to warrant such an attempt to crystallize the situation.

Yours faithfully,
W. F. G. Swann.

Department of Physics,
University of Minnesota, U.S.A.
March 8th, 1923.

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